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Recovery of Calcium Carbonate and Sulfur from FGD Scrubber Waste

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16. ABSTRACT The report gives results of a demonstration of key process steps in the proprietary Kel-S process for recovering calcium carbonate and sulfur from lime/limestone flue gas desulfurization (FGD) scrubber waste. The steps are: reduction of the waste to calcium sulfide (using coal as the reducing agent), carbonation of the calcium sulfide to generate hydrogen sulfide and calcium carbonate, and recovery of precipitated calcium carbonate from inerts (coal ash). Conversion of 99% of the calcium sulfate/sulfite to calcium sulfide was achieved both in a laboratory furnace and in a pilot plant kiln. Conversion of the sulfide to carbonate and hydrogen sulfide in bench-scale equipment gave very high rates of conversion (<1% calcium sulfide remaining in the solids) and the concentration of hydrogen sulfide in the offgas typically >95%. Results of flotation, centrifugation, and filtration experiments indicate that all three methods could be used in the ash separation step, but economics favor centrifugation. Technically, the Kel-S process was shown to be ready for testing in a continuous pilot plant. However, a preliminary economic analysis of the Kel-S process, conducted by TVA for the EPA, indicated that the total cost of a limestone scrubbing FGD process using the Kel-S recovery approach was 30% higher in capital costs and 19% higher in annual revenue requirements than the W-L/Allied process.

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ABSTRACT

Key process steps in a proprietary process for recovering calcium carbonate and sulfur from lime/limestone flue gas desulfurization (FGD) scrubber waste were demonstrated. These steps comprise reduction of the waste to calcium sulfide (using coal as the reducing agent), carbonation of the calcium sulfide to generate hydrogen sulfide and calcium carbonate, and recovery of precipitated calcium carbonate from inerts (coal ash).

Conversion of 99 percent of the calcium sulfate/sulfite to calcium sulfide was achieved both in a laboratory furnace and in a pilot plant kiln. Conversion of the sulfide to carbonate and hydrogen sulfide in bench-scale equipment gave very high rates of conversion (less than 1 percent calcium sulfide remaining in the solids) and the concentration of hydrogen sulfide in the offgas typically exceeded 95 percent. Results from flotation, centrifugation, and filtration experiments indicate that all three methods could be used in the ash separation step, but economics favor centrifugation. Technically, the Kel-S process was shown to be ready for testing in a continuous pilot plant.

However, a preliminary economic analysis of the Kel-S process was conducted by the Tennessee Valley Authority (TVA) for EPA. This analysis indicated that the total cost of a limestone scrubbing FGD process using the Kel-S recovery approach was 30 percent higher in capital costs and 19 percent higher in annual revenue requirements than the Wellman-Lord/Allied Chemical process (which has been demonstrated on a commercial scale by EPA). For this reason, EPA withdrew financial support for this project.

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory (RTP), U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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SECTION 1

INTRODUCTION

Pullman Kellogg and the U.S. Environmental Protection Agency entered into Contract No. 68-02-2644 which specified that Kellogg would continue research and development of their proprietary "Kel-S" process under a joint funding arrangement. On 20 December 1978, EPA notified Kellogg that, except for this report, the contract was terminated for the convenience of the government. Kellogg had completed the first three phases of the four-phase program. This report completes Kellogg's contractual obligations to EPA.

Certain data contained in this report (mainly in the area of sludge reduction) are proprietary to Kellogg and are confidential. They have been excluded from **this report.**

The "Kel-S" process comprises a method of regenerating scrubbing sludge produced in lime/limestone flue gas desulfurization (FGD) systems. The major features of the process are: (1), production of elemental sulfur using coal as the reducing agent and process fuel and (2), recovery of calcium carbonate for recycling to the flue gas desulfurization system. The following distinct processing steps are involved:

- Reduction of lime/limestone scrubbing sludge to calcium sulfide,
- Carbonation of the calcium sulfide to generate hydrogen sulfide and calcium carbonate,

- Separation of inerts (such as coal ash, unreacted coal, limestone inerts, and other impurities) from the calcium carbonate and
- Conversion of hydrogen sulfide to elemental sulfur in a standard Claus plant.

The last step represents well-established commercial technology and is not included as part of the present study.

Two distinct inerts-separation process steps were investigated:

1. A "one step" process which consists of first converting calcium sulfide to calcium carbonate and then removing the inerts from the calcium carbonate by air flotation.
2. A "two step" process which consists of first converting calcium sulfide to calcium hydrosulfide (which is water soluble) by reaction with hydrogen sulfide, then separating the inerts by filtration or centrifugation, and finally precipitating calcium carbonate from the calcium hydrosulfide solution by reaction with carbon dioxide.

Phases I and II comprise tests for sludge reduction, calcium carbonation, calcium dissolution, inerts filtration, inerts centrifugation, and inerts flotation. Phases III and IV comprise the design, erection, and operation of a pilot plant for the calcium carbonate production and ash separation steps. The kiln, flotation, filtration, and centrifugation tests were done by subcontractors who have suitable equipment and expertise.

Reduction of sludge occurs in a rotating kiln where sludge and coal are reacted at an elevated temperature to convert calcium sulfite/sulfate compounds to calcium sulfide. Phase I involves the following steps:

1. Obtain sludge feed from a commercial SO_2 scrubbing system.
2. Dry sludge to level needed for making suitable pellets.

3. Determine suitable pelletizing procedure.
4. Determine coal content needed in pellets for complete reduction.
5. Determine feed rate for drying pellets.
6. Determine kiln operating temperature.
7. Determine kiln feed rate.
8. Perform a kiln production run to make feed for pilot plant operation.

Phase II incorporates the following tasks:

1. Bench scale carbonation tests to:
    a. Determine maximum particle size of reduced sludge that could be used to obtain suitable carbonation rates.
    b. Determine operation conditions needed to obtain maximum concentration of hydrogen sulfide in off-gas.
    c. Provide information for designing pilot plant reactors.

2. Bench scale flotation, centrifugation, and filtration tests to:
    a. Show feasibility of separating calcium compounds from coal ash and inerts.
    b. Determine range of operating conditions for pilot plant.
    c. Provide information for sizing pilot plant units.

All of the above work, with the exception of the continuous kiln production run, has been completed and the results are presented in this report.

English units were used in gathering the data for this report. Please refer to Appendix B, Metric Conversion Chart, for suitable conversion factors to metric units.

SECTION 2

SUMMARY

Under the terms of Contract 68-02-2644, Pullman Kellogg and the U.S. Environmental Protection Agency jointly funded the development of Kellogg's proprietary Kel-S process. Test work for Phases I and II was completed and results are presented in this report.

The Kel-S process comprises a method of regenerating lime/limestone scrubbing sludge from FGD systems, wherein calcium carbonate is recovered and elemental sulfur is produced using coal directly both as the reducing agent and as the process fuel. Several distinct processing steps are involved including: reduction of sludge to calcium sulfide; carbonation of the calcium sulfide to generate hydrogen sulfide and calcium carbonate; separation and rejection of inerts such as coal ash, unreacted coal, limestone inerts, and other impurities; and conversion of hydrogen sulfide to elemental sulfur in a standard Claus plant. Since the last step involves well-established commercial technology, it is not included in the present development.

Two distinct inerts separation process steps were investigated:

1. A "one step" process which consists of first converting calcium sulfide to calcium carbonate and then removing the inerts from the calcium carbonate by air flotation.
2. A "two step" process which consists of first converting calcium sulfide to calcium hydrosulfide (which is water soluble) by reaction with hydrogen sulfide, then separating the

inerts by filtration or centrifugation, and finally precipitating calcium carbonate from the calcium hydrosulfide solution by reaction with carbon dioxide.

Phase I involved reduction of scrubbing sludge in both bench scale and pilot-sized equipment and included pelletizing and drying studies. Phase II included carbonation, dissolution, centrifugation, filtration, and flotation, using bench scale tests only. The bench scale reduction, carbonation, and dissolution tests were carried out by Kellogg at its R&D Center, Houston, Texas, and the kiln, flotation, centrifugation, and filtration tests were done by subcontractors who have appropriate equipment and expertise.

Based on Kellogg in-house data previously obtained in bench scale equipment, pellet compositions were specified for the initial kiln test work. Using these compositions, a pelletizing procedure was developed which produced pellets strong enough to be used in rotary kiln operations. The pellets were produced by mixing about 4% bentonite binder with the dried coal/sludge material and then spraying a 5 wt % starch (in water) solution on the pellets as they were formed.

The green (wet) pellets were dried in a pilot flowdryer that kept the pellets agitated above a grate through which hot air (270°F) flowed. Attempts to run the dryer continuously were unsuccessful; therefore, batch drying was used. The dried pellets were collected in drums and stored prior to kiln processing.

Using the dried pellets, kiln tests were made to establish the operating conditions necessary to achieve a maximum reduction of the sludge. Essentially complete reduction of the calcium sulfate/sulfite compounds to calcium sulfide was achieved.

The pelletizing procedure produced pellets of variable quality because spraying the starch solution on the pellets was done manually and was difficult to control in below freezing weather. Kennedy Van Saun (KVS) tested several mixtures of materials and concluded that satisfactory pellets could be produced by pelletizing mixtures containing 2% bentonite and 2% wheat starch.

Bench scale reduction tests were carried out by Kellogg in a laboratory furnace to expand the data base obtained in the KVS kiln tests. These results confirmed the pilot kiln results and the minimum amount of coal required for complete reduction.

Using the reduced material produced in the KVS kiln tests, Kellogg carried out bench scale carbonation tests to define operating conditions and produce a feed for the air flotation tests in order to determine whether calcium carbonate could be separated effectively from impurities. The bench scale carbonation tests indicated that the conversion of calcium sulfide to calcium carbonate and hydrogen sulfide was extremely rapid and apparently limited by the rate at which CO_2 could be fed into the system. Concentration of H_2S in the effluent gas ranged from 90% to 100%, for most of the runs, which is ideal feed gas to a Claus plant.

The effect of particle size of the reduced sludge was studied using -12 to +140 mesh, and -140 mesh particle-size distributions, but the results were not conclusive. It appears that particle size within the range tested is not critical. The effects of pressure and temperature also were evaluated, but within the range tested (20 psig to 60 psig, 150° to 250° F), no significant differences were observed.

Product produced in the Kellogg bench scale carbonation tests was used in the air flotation tests performed at Denver

Equipment facilities in Denver, Colorado. It was determined that three additives (fuel oil, pine oil, and a proprietary promoter manufactured by American Cyanamid) and three floats were needed to achieve about 75% recovery of calcium carbonate and approximately 50% inerts rejection. These results indicate that air flotation could be used commercially.

Although air flotation was shown to be technically feasible, the air flotation additives which remained with the recovered ash might preclude the use of the recovered ash as landfill owing to environmental regulations. Significant amounts of calcium carbonate (25%) would also be rejected with the ash. It was then decided to examine the use of filtration and centrifugation to remove ash from the system.

The "two step" process consisted of:

1. Dissolving calcium sulfide by adding hydrogen sulfide thus forming soluble calcium hydrosulfide
2. Removing the insoluble ash by filtering or centrifugating
3. Precipitating the calcium as calcium carbonate from solution by adding carbon dioxide.

Kellogg did some bench scale semi-batch-type (i.e., continuous gas flow, batch liquid/solids) tests which demonstrated the calcium dissolution and calcium carbonation steps. The maximum percent H_2S generated in the carbonation step ranged from 86-98% H_2S which is ideal for sulfur plant feed. The precipitated $CaCO_3$ was extremely pure (99.37%), and should be excellent recycle to a limestone scrubbing unit.

The two-step intermediate product (ash and dissolved calcium/sulfur values) was sent to the Bird Machine Company for centrifuge and filter tests. Both the centrifuge and filter tests indicated better calcium recovery and less calcium rejection than from the air flotation units. Using the data from these tests, Kellogg did a process evaluation to compare the relative merits of the one-step and two-step processes. Results showed that although the air flotation units have the lowest capital cost, the penalties of lower separation efficiency and potentially polluting additives makes air flotation less attractive than filters or centrifuges. Centrifuges are preferred over filters because of lower capital costs.

As a result of this economic analysis, the pilot plant design was changed to use the two-step process and to incorporate a centrifuge as the ash separation device.

SECTION 3

CONCLUSIONS/RECOMMENDATIONS

All steps in Phases I and II, except for the kiln run to produce feed material for the pilot plant, were completed. Sludge was reduced satisfactorily in all three kiln test runs. The temperature profile in the kiln and pellet retention time for each pellet composition are significant variables affecting sludge reduction. Results from the three kiln runs show conclusively that the run to produce pilot feed material can be made with complete confidence that satisfactory reduction will be achieved.

Carbonation tests conducted with the bench scale reactor show that the rate of conversion of sulfide to carbonate and H_2S is rapid, and that high purity levels of H_2S in the effluent gas are achieved.

Flotation, filtration, and centrifugation experiments indicated that centrifugation is the preferred method of ash rejection.

The objectives of Phases I and II were successfully demonstrated. Therefore, it would be technically sound to proceed with Phase IV, erection of the pilot plant.

SECTION 4
DISCUSSION OF RESULTS

4.1 SLUDGE REDUCTION

4.1.1 Sludge Production

To evaluate the potential of Kel-S to convert lime/limestone scrubbing sludge into sulfur and limestone properly, it is necessary to use a feed sludge typical of that produced in a commercial scrubbing system. Based on many years of experience with pilot plant operation and considering such process factors as minimum liquid velocities (to avoid solids settling in transfer lines), mass transfer requirements, length of operation, etc., it was estimated that about 30 to 40 tons of sludge solids would be needed for the proposed project. With this as a goal, a search was undertaken to find a suitable source of scrubbing sludge. It should be noted that at the time (mid-1975), very few scrubbers were in operation, especially ones that were producing sludge suitable for Kel-S feed; i.e., sludge free of other material such as fly ash or stabilizing additives. One potential source was TVA's Shawnee plant, but this is an experimental unit which is deliberately operated under a variety of conditions, hence, the product sludge varies considerably. Ultimately, it appeared that Commonwealth Edison's, Will County Station scrubber was producing sludge that, prior to treating, came closest to meeting Kel-S requirements. Personnel at the Will County (Illinois)

Station were contacted and they agreed to supply Kellogg with scrubber sludge.

Based on telephone conversations with Will County personnel, it appeared that the solids content of the effluent slurry was between 30% and 40%. Therefore, 100 tons of slurry was chosen as the quantity needed to ensure adequate supply feed for the Kel-S Project. Arrangements were made to ship approximately 100 tons of material from Will County to Allis Chalmers' test center located in Oak Creek, Wisconsin. At that time, tentative agreement had been reached with Allis Chalmers whereby they, as a subcontractor, would supply the necessary equipment, manpower, and expertise needed to process the sludge through the pelletizing and reduction steps required for Kel-S. Sludge was shipped by tank truck to Oak Creek and impounded in an outside reservoir comprising a concrete pad enclosed by curbs.

Under the original schedule, it was planned to carry out the kiln tests shortly after the sludge was obtained. Problems were encountered in negotiating a contract with Allis Chalmers and, finally, they withdrew from the project. A search for a new subcontractor was undertaken and eventually Kennedy Van Saun (KVS) agreed to participate, and a contract was signed.

When the Kennedy Van Saun contract was signed, the sludge, which had been stored outside, had lost water through evaporation and was suitable for shipping as a dry product. Accordingly, the dried sludge, totaling about 35 tons, was loaded into steel drums and trucked to Kennedy Van Saun's test center located at Danville, Pennsylvania. Subsequently, it was found that the long exposure to air had oxidized the sulfite to sulfate and, further, the apparent average particle size had increased either by crystal growth or by agglomeration. In any event, the coal/sludge pellets formed by the previously established procedure were too weak for kiln feed and a new technique had to be developed.

4.1.2 Pelletizing

4.1.2.1 Background.- The sludge was dried in open air and was, therefore, not uniform. It had variations from 3% to 15% H_2O, as determined by KVS, and from 5% to 10% H_2O, as measured by Kellogg. KVS analyzed a larger number of samples for water than Kellogg did which accounts for the different range of values reported.

When the sludge arrived at KVS, Kellogg took samples from four different drums. These samples were brought to the Kellogg R&D Center for analysis. Table I shows the results of the analysis and indicates that nearly all of the original $CaSO_3$ content was oxidized to $CaSO_4$ during the 2 years of open-air storage. The trend of this oxidation is shown in Figure 1.

Kennedy Van Saun conducted a study of the pelletization properties of sludge/coal mixtures. The pellets were tested for strength by two common methods:

- Drops; the number of 18" drops onto a steel plate until breaking
- Compression strength; four pellets were placed between two steel plates and additional weights were added until one or more of the pellets broke.

TABLE I.- SLUDGE ANALYSIS AS RECEIVED AT KENNEDY VAN SAUN 9 SEPTEMBER 1977

Sample Component	Sample			
	A-1 wt%	A-2 wt%	B-1 wt%	B-2 wt%
$CaSO_4.2H_2O$	53.7	57.1	51.9	54.6
$CaSO_3.1/2H_2O$	2.9	0.6	4.1	0.8
$CaCO_3$	31.5	24.9	31.6	26.0
Inerts	5.9	6.4	5.9	6.1
Air dry loss	5.6	10.9	5.4	9.3

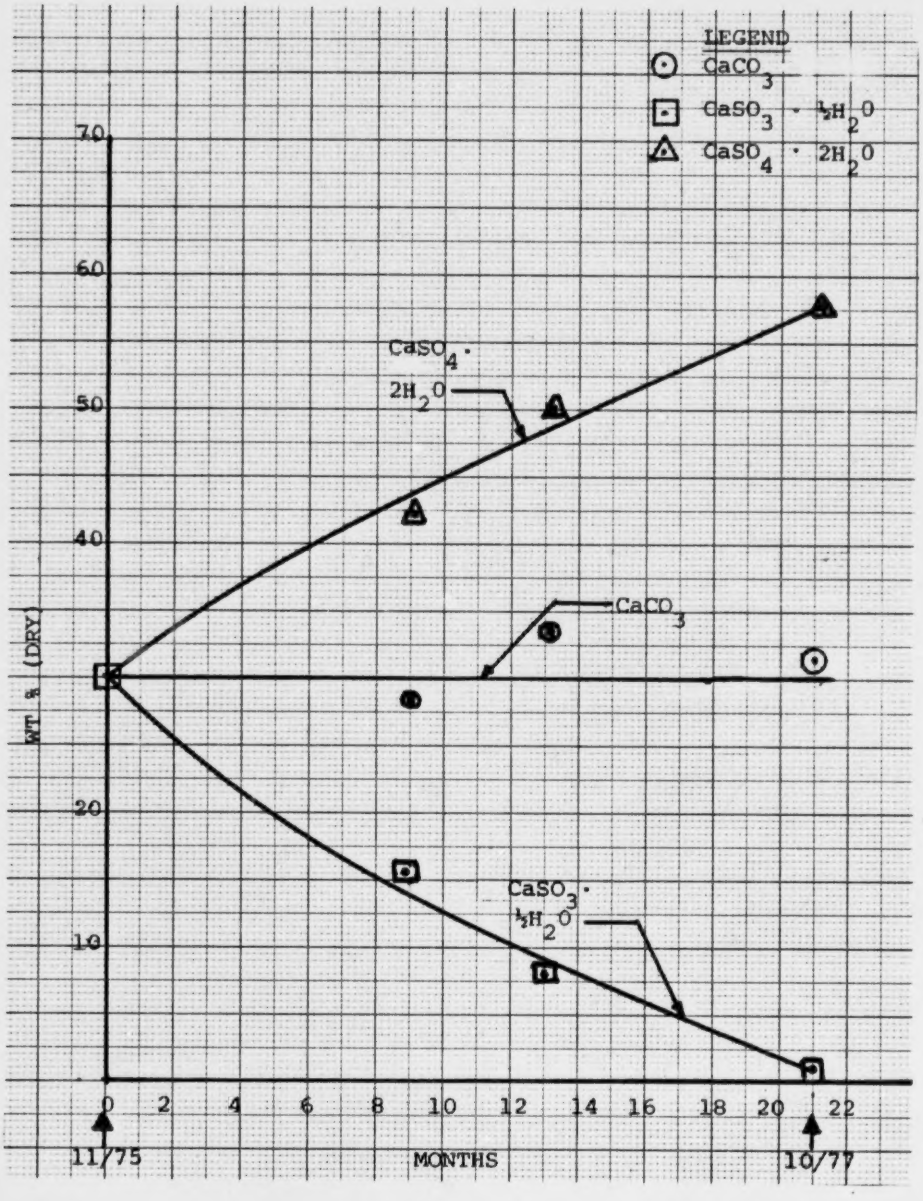

Figure 1.- Kel-S scrubber sludge, effect of storage.

Their initial work produced pellets with low wet compression strength (2 lb)*, low dry compression strength (2 lb), and a low number of 18-in. drops onto a steel plate to breakage (5 wet and 1.5 dry). KVS felt that the pellets were not strong enough to survive drying or kiln processing and suggested that a binder be added to the mix for increased strength. Original process verification, conducted at Allis-Chalmers, indicated that the sludge/coal mixtures pelletized into suitable pellets.

We, therefore, requested that Allis Chalmers confirm the results of KVS laboratory tests. The work conducted by Allis-Chalmers essentially confirmed the results obtained by KVS (1.5 lb wet strength, 1.0 lb dry strength, and 5.5 wet drops). Both laboratories concluded that the pellet strength should be increased by adding bentonite (a common pelletizing additive) and by grinding the sludge prior to pelletization. KVS also suggested spraying a starch/water solution on the pellets during pelletization for added strength. A copy of a report prepared by Allis-Chalmers describing pelletization studies on the Will County Sludge is contained in Appendix A.

The results from both pelletization studies indicated that the scrubber sludge was difficult to pelletize for the following major reasons:

1. The Will County scrubber sludge was stored for 2 years and the particle size had increased.

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*Although it is EPA policy to use metric units, the English units used in this report were used in gathering the data. Refer to Appendix B, Metric Conversion Chart.

Grinding was required to reduce the sludge to a particle distribution similar to that of the sludge which had previously produced suitable pellets.

2. The compositions of the two sludges were drastically different. The original sludge used in the Kel-S process development contained an unusually high amount of flyash (37.35 wt %). To decrease the percentage of flyash and increase the sulfur content of the sludge, agricultural gypsum was added to the scrubber sludge to make a synthetic sludge mixture. The commercial gypsum was ground finely which generally contributes to the production of strong pellets. This modified sludge was easy to pelletize and produced pellets with dry strengths to 15.8 lb, wet strengths to 5.2 lb, and up to 20+ wet drops before breakage occurred. These characteristics made the pellets satisfactory for drying and kiln processing. The Will County sludge contains about the same amount of $CaSO_4$ as the original mixture, but as it has a drastically different origin, it also has different pelletization properties.

Kennedy Van Saun was asked to undertake a program to develop a method of producing pellets that could survive drying and kiln processing. They determined by testing that bentonite should be mixed with the coal and sludge prior to pelletizing such that the dry mixture contained 4 wt % bentonite and that a starch solution should be sprayed on the pellets during pelletizing. This starch solution consisted of 5 wt % starch in water, and it was sprayed on separately from the water pelletization spray. The sludge also had to be ground to pass through a 100 mesh (149 microns) sieve prior to pelletizing. This procedure produced pellets from a laboratory pelletizer with a wet strength of 4 to 6 pounds, +24 drops wet, and +24 drops dry. Pellets of this strength can survive drying and kiln processing.

4.1.2.2 Composition and procedure.- Three different coal/sludge mixtures were prepared (about 5,000 lb each for three different kiln runs) to determine the best coal content of the pellets for $CaSO_4$ reduction. The results of the kiln runs determined the coal content of the production kiln runs. Mixture K1 was prepared in November, 1977; mixtures K2 and K3 were prepared in January, 1978. All three mixtures contained 4% bentonite, a specified amount of coal, and less than 1% starch solution. The balance was ground sludge.

The coal used in the test was Western Kentucky #9. An analysis is given in Table II. The coal was ground in the Kennedy Van Saun, air-swept, ball-mill system until 90% passed 100 mesh. A particle size distribution is given in Figure 2.

The sludge was ground in the air-swept, ball-mill system to break up the agglomerates; it was difficult to grind due to its moisture content. The sludge probably would not have to be ground in a commercial plant since the agglomerates appear to have resulted from the open air storage.

The bentonite was "western bentonite" which was very fine as received and did not require grinding.

TABLE II.- COAL ANALYSIS, WESTERN KENTUCKY #9
(AS RECEIVED BASIS)

Proximate Analysis	
% Moisture	2.33
% Ash	10.20
% Volatile matter	36.80
% Fixed carbon	50.67
Ultimate Analysis	
% C	69.41
% H	5.19
% N	1.68
% Cl	0.03
% S	3.66
% O (by difference)	7.50
Heating Value - BTU/lb.	12,746

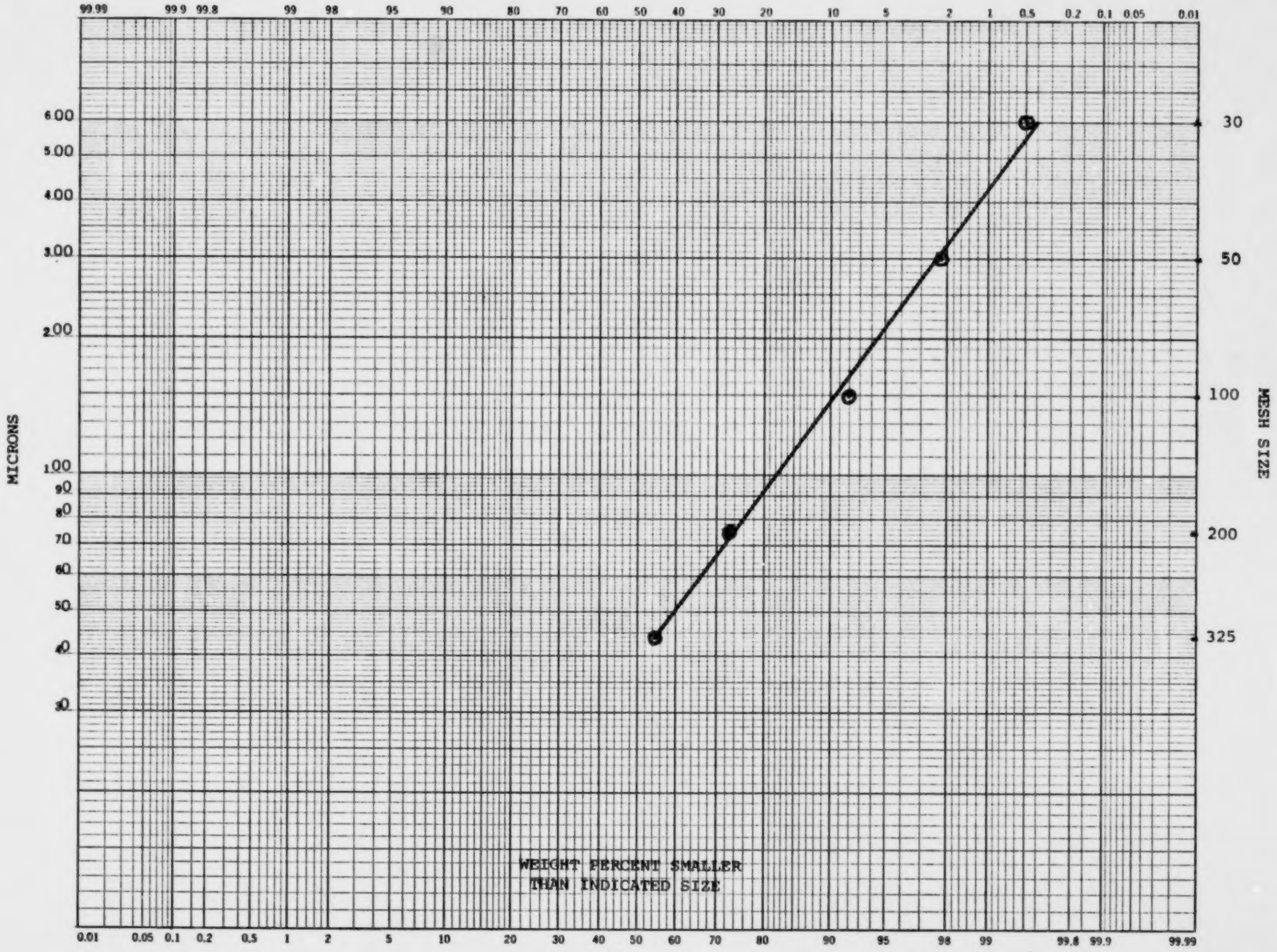

Figure 2.- Particle size distribution - Coal.

The coal, sludge, and bentonite were weighed out and mixed together in 200-lb batches. The mix was then put in a hopper and continuously fed by a screw feeder into a 4-ft-diameter cone pelletizer. Pelletizing water was sprayed into the pelletizer at the point where the pellets began to form. Starch solution was then sprayed onto the pellets before they exited the cone. The pellets dropped out of the pelletizer into a wheelbarrow. When the wheelbarrow was filled, the pelletizer was stopped, the wheelbarrow emptied, and then the pelletizer restarted. The pellets were stored on a concrete floor prior to drying (usually overnight). Wet pellets contained about 20% moisture.

4.1.2.3 Pellet drying.- A travelling grate kiln was originally specified at Allis Chalmers for pellet drying to minimize damage to the wet pellets during drying.

Kennedy Van Saun did not have a pilot plant size grate kiln and originally suggested that the rotary kiln preheater be used as a dryer. (See Figure 3.) The preheater is an integral part of the rotary kiln. The pellets are dried by the hot kiln exit gases in the preheater and leave the preheater by means of a hydraulic ram. Once the pellet properties were known, it was decided that the wet pellets would probably not feed through the kiln preheater cone bottom and that the preheater ram would severely damage the dry pellets. KVS then suggested the use of their pilot flowdryer system (Figure 4) for pellet drying. The dried pellets could then be fed into the kiln by a belt feed, minimizing pellet breakage.

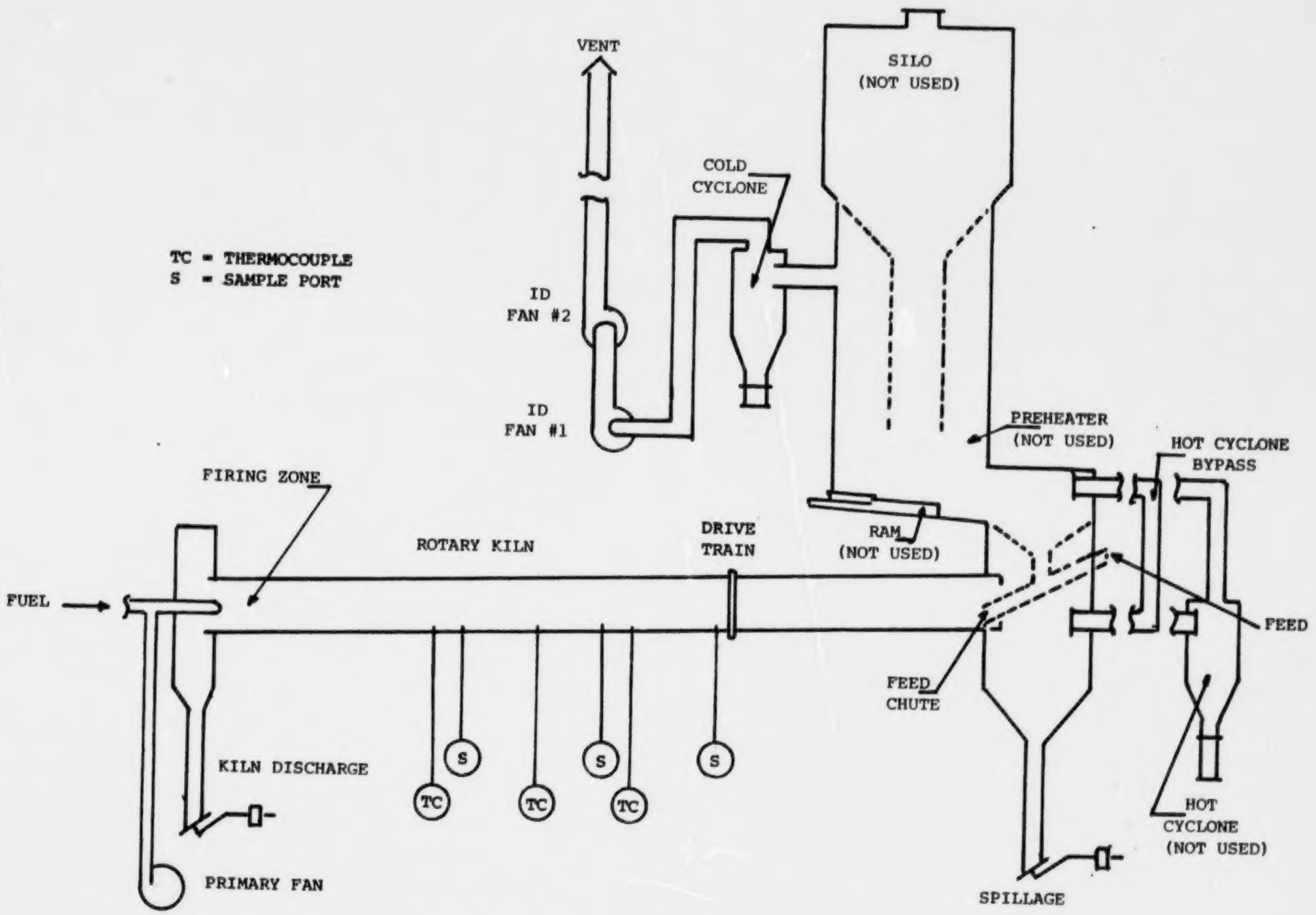
VENT
SILO
(NOT USED)
COLD
CYCLONE
TC = THERMOCOUPLE
S = SAMPLE PORT
ID
FAN #2
ID
FAN #1
PREHEATER
(NOT USED)
HOT CYCLONE
BYPASS
FIRING ZONE
ROTARY KILN
DRIVE
TRAIN
RAM
(NOT USED)
FUEL
FEED
FEED
CHUTE
S
S
S
KILN DISCHARGE
TC
TC
TC
HOT
CYCLONE
(NOT USED)
PRIMARY FAN
SPILLAGE

Figure 3.- KVS 24-inch OD by 30-foot rotary pilot kiln.

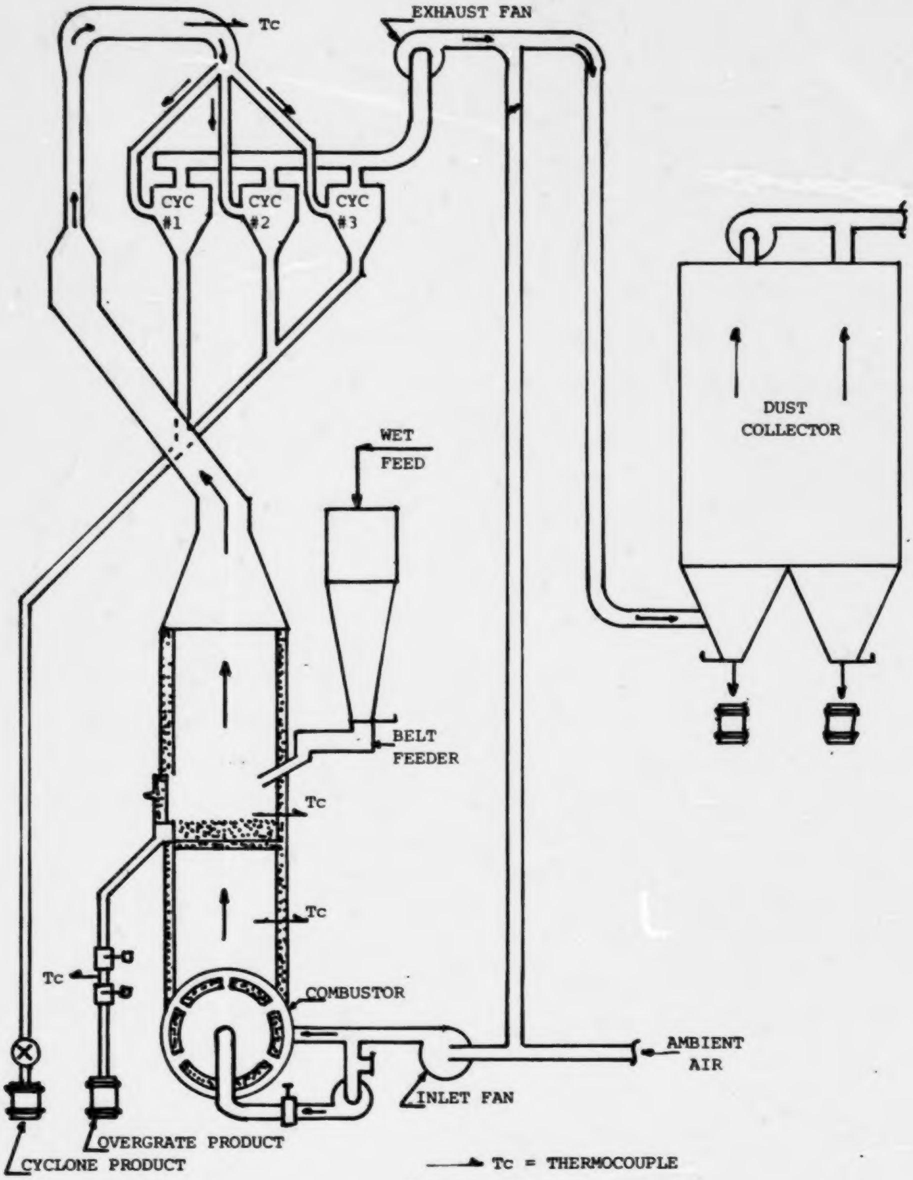
Tc
EXHAUST FAN
CYC #1
CYC #2
CYC #3
DUST COLLECTOR
WET FEED
BELT FEEDER
Tc
Tc
Tc
COMBUSTOR
AMBIENT AIR
INLET FAN
OVERGRATE PRODUCT
CYCLONE PRODUCT
Tc = THERMOCOUPLE

Figure 4.- Pilot flowdryer system.

The pellets were conveyed by bucket elevator to a bin above the flowdryer, from which they were belt-fed to the flow dryer. Drying was achieved on a batch basis at about 270° F. Pellets were fed into the flowdryer to a depth of about 12 in. over a fixed grate, and then contacted with hot air flowing upwards through the grate for about 10 min. The pellet bed did not expand much, although the pellets were well mixed by the fluidizing air. An attempt was made to dry the pellets continuously, but then the pellets did not stay above the grate long enough to dry completely. Therefore, all pellets were dried on a batch basis.

The dried pellets were collected in drums and stored prior to kiln processing.

4.1.2.4 KVS pelletizing study.- The pellets for the kiln runs K1, K2, and K3 were all prepared using the procedure described in Section 4.1.2.2. This procedure produced suitable pellets for kiln run K1, but did not produce suitable pellets for the K2 and K3 kiln runs, probably due to the severe weather conditions (sub-zero) at Danville during the pelletizing, which made spraying of the starch solution difficult.

A bench scale pelletization study was then performed at Kennedy Van Saun to develop a better pelletization technique to use in future production pelletization runs. The best procedure found was to add 2% bentonite and 2% wheat starch to the sludge/coal mixture before pelletizing. This procedure produced about the same strength pellets as the previous procedure (4 wt % bentonite and spraying a starch solution on formed pellets) but is easier to control and should produce consistently strong pellets.

The results of eight pelletization tests are given in Table III. Test 1 simulates the procedure used in the kiln pilot plant runs. This procedure produces acceptable pellet strengths, but does not result in uniform pellet strengths since a starch solution must be sprayed by hand on the formed pellets. Starch was added to the dry mix before pelletization in Test 2 and produced strengths similar to Test 1. This method of dry starch addition would be much simpler in the pilot plant pelletizer.

Tests 3 through 6 investigated four different additives, lime, plaster of Paris, sodium silicate, and ground reduced sludge from a previous kiln run. The sodium silicate was added with the pelletizing water. All four tests resulted in pellets having unacceptable dry strength.

Test 7 increased the dry starch content and decreased the bentonite content, as compared to Test 2, and this resulted in an increase in the number of wet drops, but did not change the other results. The procedure of Test 7 is recommended for use in the pilot plant pelletizer. Test 8 was done to determine how much effect the coal content had on pellet strength. The reduced coal content decreased the number of wet drops, but increased the number of dry drops. The pellets of Test 8 still have an acceptable strength for kiln processing.

TABLE III.- PELLETIZING STUDY - KENNEDY VAN SAUN

Test Number	Wet Drops	Wet Compression Pounds	Dry[1] Drops	Dry[1] Compression Pounds	Additives
1[2]	11	6.5	18.5	17.0	4% Bentonite added, pellets coated with starch solution
2[2]	11	3.5	13.5	+21.0	4% Bentonite + 0.5% starch (dry)
3[2]	4.0	3.0	0	0	5% Lime
4[2]	4.5	5.0	1.0	2.0	5% Plaster of Paris
5[2]	3.5	1.5	1.0	2.0	Pelletized with 20% sodium silicate solution
6[2]	4.0	6.0	1.0	2.0	5% ground reduced sludge (kiln discharge)
7[2]	18.0	4.0	13	+21	2% Bentonite, 2% starch
8	13.0	4.0	+40.0	+21.0	2% Bentonite, 2% starch

[1] Dried at 120° C

[2] Tests 1-7 all contained the same weight % coal.

[3] Test 8 contained a lower weight % coal.

4.1.3 Kiln Tests

4.1.3.1 Apparatus/procedure.- The sludge was reduced in an oil-fired rotary kiln; however, it would be coal-fired in a commercial operation to avoid the need for maintaining a supply of fuel oil. Kennedy Van Saun has an existing oil-fired, 24-in.-diameter by 30-ft-long kiln which was used for these tests. The objective was to define operating conditions for the continuous production run to ensure that essentially complete reduction of the sludge would be obtained. It was decided to use three different levels of coal in the pellets and to operate the kiln at conditions which would achieve maximum reduction for each mixture. Analysis of kiln offgas and product solids was used to set operating conditions.

The ideal condition would have been a continuous flow of the freshly made pellets through the reduction kiln. In such an arrangement, adjustments in the composition of the pellets could be made while the reduction step was being carried out.

Such a process sequence could not be realized at Danville because the operators who conducted the pelletization step also ran the kiln pilot plant. It was, therefore, decided to pelletize enough material for a 2-day kiln run, dry it, and store it as feed for the rotary kiln. (See Figure 3.)

A gas sampling connection was installed at the kiln outlet; this led to a gas chromatograph and an SO_2 analyzer located in a shed near the firing end of the kiln.

The instruments were used for continuous gas analysis of CO, CO_2, N_2, O_2, CH_4 and higher hydrocarbons, H_2, H_2S, and SO_2. In addition, KVS used an Orsat gas analyzer to provide readings of CO, O_2, and CO_2 at an independent sampling point. An optical pyrometer was used to read kiln temperature in the firing zone; thermocouples were provided at 9, 13, and 16 ft from the firing end; sample ports were provided 10, 15, and 20 ft from the firing end.

The kiln was operated at 2 rpm and with a slope of 3/8 in./ft. The hot end temperature (1,750° F) was supposed to be maintained. The nominal feed rate selected was 175 lb/hr. The oil rate varied between 5 and 6 gph during the kiln runs.

4.1.3.2 Mixture K1 pellets.-

A. Conditions of run - During the first day of operation, it became obvious that the optical pyrometer readings had to be maintained above 1,750° F to reach reaction temperatures in the hottest zone of the kiln. This is shown in Figures 5 and 6. Gas analyses recorded during the period are shown in Tables IV and V. Reaching stable operating conditions in the kiln took from 10 a.m. until 3 p.m. on the 21st, at which time the reducing atmosphere in the kiln was fully established. On the second day, lining-out of the kiln took from 9 a.m. to 11 a.m. However, because of several power supply failures, the analytical results were affected as well as was the kiln firing. The feed rate on the second day was

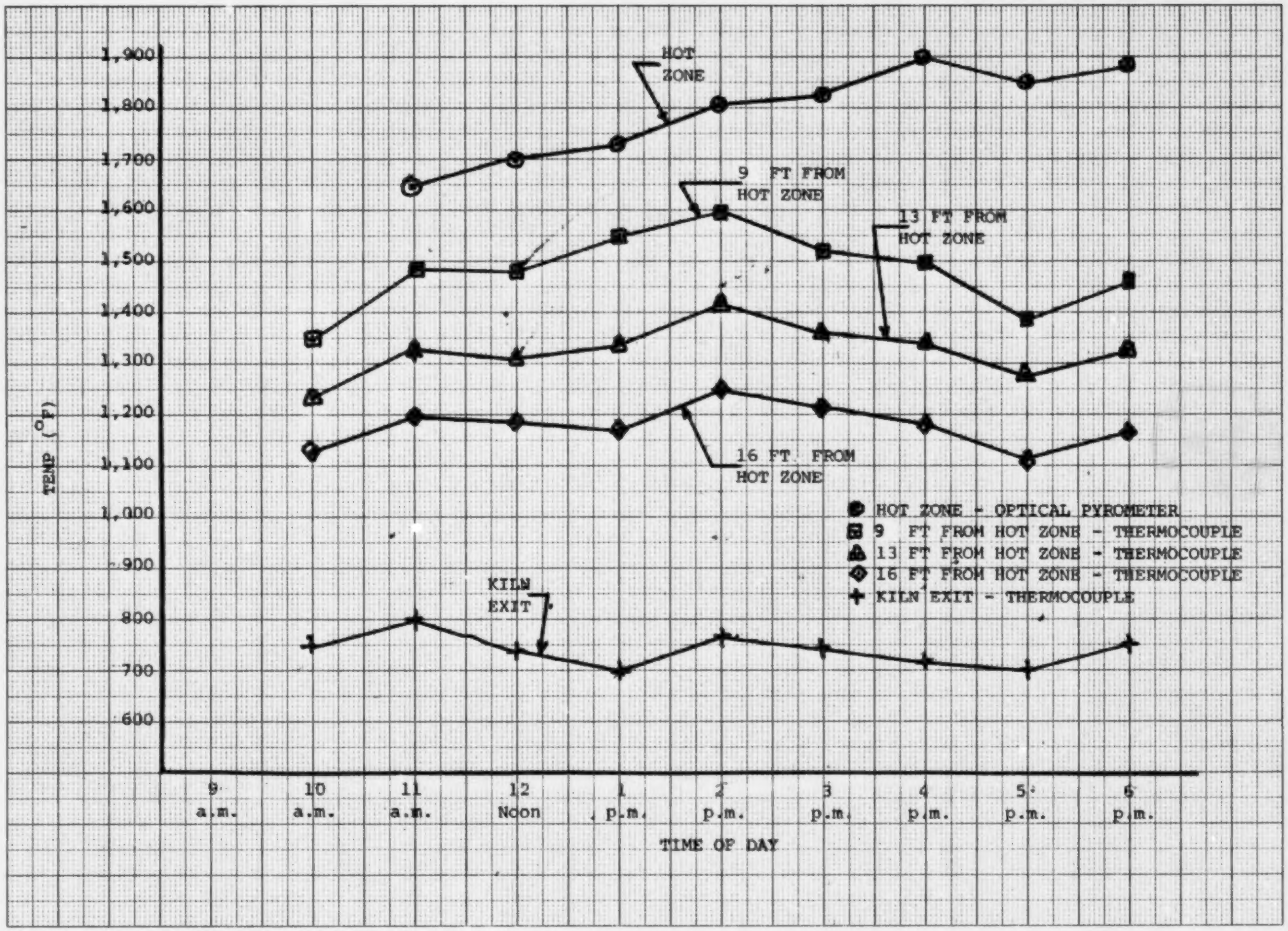

Figure 5.- Time-temperature profiles, mixture K1 kiln test, 11/21/77.

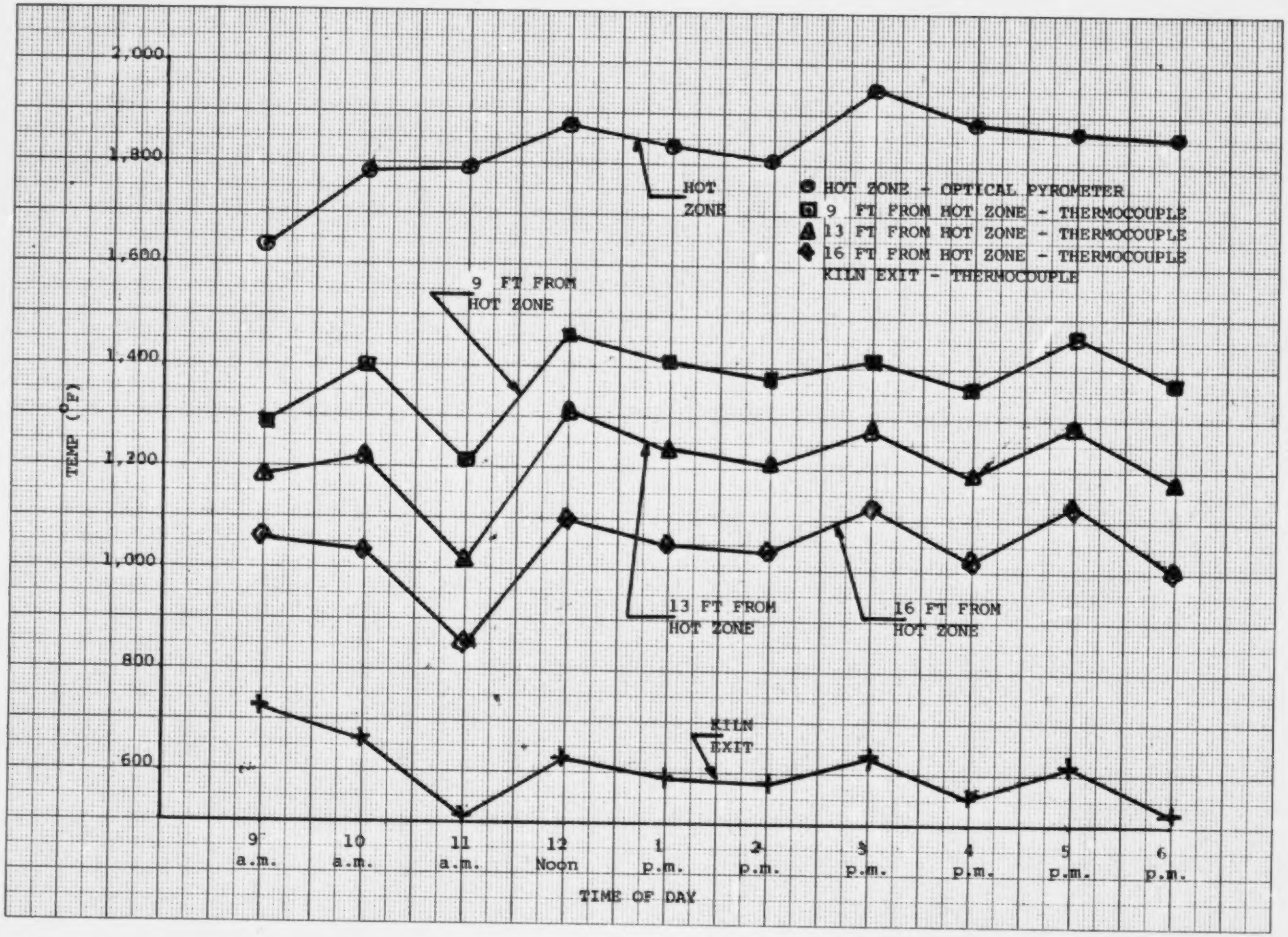

Figure 6.- Time-temperature profiles, mixture K1 kiln test, 11/22/77.

TABLE IV.- GAS ANALYSES FROM KVS KILN (21 NOVEMBER 1977)

Time of Day	Samples				
	H_2S (mol %)	$^*O_2$ (mol %)	N_2 (mol %)	$^*O_2$ (mol %)	SO_2 (ppm)
1008	--	--	--	--	572
1032	--	--	--	1.99	619
1040	--	--	--	1.76	--
1053	--	--	--	2.53	--
1102	N/D	1.94	78.70	--	850
1130	N/D	0.89	77.14	--	--
1150	--	--	--	2.57	--
1152	N/D	2.03	77.21	--	1034
1303	>250	1.14	75.42	0.71	--
1315	--	--	--	0.80	--
1326	--	--	--	0.81	--
1332	>250	0.77	75.93	--	702
1343	--	--	--	0.75	--
1358	>250	0.69	76.54	0.80	250
1420	--	--	--	0.71	--
1440	--	--	--	0.79	--
1446	>250	0.69	74.95	--	250
1512	>250	0.77	74.78	0.84	--
1523	--	--	--	0.80	--
1545	--	0.62	72.32	--	--
1610	>250	0.62	71.35	--	--
1637	>250	0.72	68.90	--	--

*Oxygen was taken by two different instruments as a consistency check.

N/D - Not detected

TABLE V.- GAS ANALYSES FROM KVS KILN (22 NOVEMBER 1977)

Time of Day	Samples				
	H_2S (mol %)	*O_2 (mol %)	N_2 (mol %)	*O_2 (mol %)	SO_2 (ppm)
0938	--	--	--	0.76	--
0946	--	--	--	0.80	--
1000	--	--	--	0.80	--
1016	--	--	--	0.80	--
1045	--	--	--	--	131
1104	--	--	--	0.95	--
1109	>250	0.71	71.21	--	--
1140	>250	0.66	71.21	0.79	--
1204	--	--	--	0.79	96
1215	>250	0.66	73.88	--	--
1231	--	--	--	0.79	--
1249	>250	0.71	76.18	--	--
1314	--	--	--	0.74	--
1328	>250	0.60	69.64	--	--
1330	--	--	--	0.73	--
1416	--	--	--	0.93	--
1418	>250	0.83	76.55	--	--
1440	--	--	--	0.75	--
1456	--	--	--	0.82	--
1500	>250	0.66	70.38	--	--
1511	--	--	--	--	33
1512	--	--	--	0.78	--
1543	>250	0.51	60.35	--	--

*Oxygen was taken by two different instruments as a consistency check.

TABLE V.- GAS ANALYSES FROM KVS KILN
(22 NOVEMBER 1977) (Contd.)

Time of Day	Samples				
	H_2S (mol %)	*O_2 (mol %)	N_2 (mol %)	*O_2 (mol %)	SO_2 (ppm)
1625	--	--	--	2.75	--
1635	--	--	--	0.80	--
1646	--	--	--	0.76	--
1654	>250	0.66	69.72	--	--
1657	--	--	--	0.80	--
1700	--	--	--	0.79	--
1724	>250	0.60	68.56	--	--
1750	--	--	--	--	41
1806	>250	0.57	64.74	--	--
1832	>250	0.60	64.34	--	--

*Oxygen was taken by two different instruments as a consistency check.

increased from 175 lb/hr to 182 lb/hr at 1 p.m. With the higher feed rate, the stability of operation of the kiln was improved. The reducing atmosphere in the kiln was easily maintained, and the temperature gradient through the kiln was increased which gave better performance.

The only problems encountered were with the kiln exhaust gases which contained some 3,000 ppm of H_2S and coal dust. In an industrial plant these gases are used as fuel, and H_2S is recovered by amine scrubbing and processed to elemental sulfur in a Claus plant; in the pilot plant, some means of treatment of the gas will have to be found.

B. Results - The results of the reduction step are best seen in Table VI. KD gives the analyses of the kiln discharge, the Port 1 material in the kiln 10 ft from the discharge, and the Port 3 material at 16 ft from the kiln discharge. Of the seven KD samples analyzed, five had reductions of 99 mol% or better. The two below 99% (97.7% and 95%) were obtained during the first day, with "low" rate of kiln feed. Figure 7 plots the percent reduction as a function of the temperature of the sample point of the furnace. At first glance, interpretation of these data is difficult. Looking, however, at the temperature of the Port 1 level one hour before the kiln discharge sample was taken, showed that the 99% reduction data had temperatures of 1,400° to 1,450° F, while the 95% reduction sample showed 1,550° F and the 97.7% showed 1,520° F. The two

TABLE VI.- KEL-S PILOT PLANT ANALYSES - MIXTURE K1 KILN TEST
(21, 22 NOV 1977)

Sample Description	Time Sample Taken	Date Sample Taken	CaS (wt %)	$CaSO_3$ (wt %)	$CaSO_4$ (wt %)	$CaCO_3$ (wt %)	CaO (wt %)	Al_2O_3 (wt %)	FeO (wt %)	MgO (wt %)	Free Carbon (wt %)
KD	2 p.m.	11/21/77	41.07	3.23	0.46	0.89	26.49	2.70	2.74	0.93	2.66
Port 1	2 p.m.	11/21/77	38.56	0.60	0.61	3.65	23.67	2.88	2.63	0.75	7.80
KD	4 p.m.	11/21/77	38.38	1.35	0.20	0.0	25.51	2.00	1.83	0.67	1.49
Port 1	4 p.m.	11/21/77	40.05	0.0	0.21	3.06	23.10	2.64	2.51	0.79	9.92
Port 3	4 p.m.	11/21/77	1.30	0.15	39.15	21.15	4.60	0.51	0.89	0.30	--
KD	6 p.m.	11/21/77	42.83	0.30	0.48	0.28	23.25	2.44	2.08	0.72	1.64
Port 1	6 p.m.	11/21/77	38.10	0.15	0.59	4.68	23.72	2.60	2.26	0.69	10.29
KD	11 a.m.	11/22/77	41.07	0.0	0.85	0.69	26.74	2.92	2.53	0.79	4.32
Port 1	11 a.m.	11/22/77	6.40	0.0	32.87	20.67	8.63	1.31	1.61	0.44	12.43
KD	2 p.m.	11/22/77	42.59	0.30	0.0	0.57	25.72	3.20	2.89	0.84	5.27
Port 1	2 p.m.	11/22/77	18.45	0.0	15.48	20.94	10.32	1.94	1.81	0.58	11.67
KD	4 p.m.	11/22/77	43.48	0.0	0.72	1.06	22.45	2.86	2.53	0.82	4.21
Port 1	4 p.m.	11/22/77	25.77	0.0	13.84	18.91	8.41	1.95	1.76	0.58	10.64
Port 3	4 p.m.	11/22/77	1.21	0.0	39.57	19.15	4.43	0.44	0.73	0.32	--
KD	6 p.m.	11/22/77	37.91	0.30	0.51	2.18	24.86	2.68	2.27	0.77	7.66
Port 1	6 p.m.	11/22/77	21.88	0.0	11.93	17.07	12.13	1.86	1.59	0.58	12.71

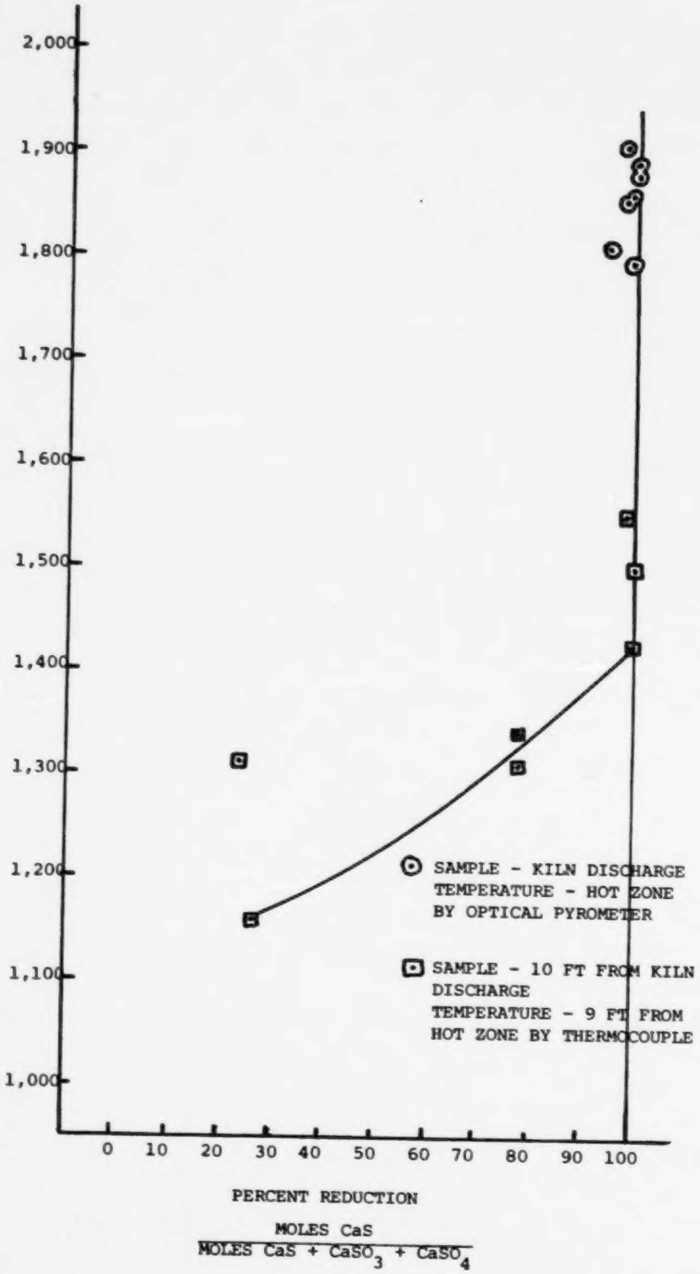

Figure 7.- $CaSO_x$ reduction - Temperature profiles, mixture K1 kiln tests, 11/21/77 and 11/22/77.

samples with the lower conversion both showed high $CaSO_3$ content, while the $CaSO_4$ content remained low in all samples. Therefore, the probable cause of the limited reduction was reoxidation of the sulfide. Because of the design of the kiln burner, there was an excess of oxygen in the firing zone, and reoxidation of the sulfide was possible. Most of the calcium carbonate present in the sludge was converted to oxide in the kiln, as expected.

An interesting phenomenon was the presence of excess carbon in the reduced pellets. No single factor would explain this, but it was affected by the quality of the pellets, temperature profile in the kiln, and the residence time of the pellets in the kiln. Because of the limited time of experimental kiln operation, it was impossible to develop conditions for full utilization of the process coal.

4.1.3.3 Mixture K2 pellets.- The pellets for this run and the 12% run were prepared on January 9th to 13th and were stored in barrels for the reduction step. The pelletization step was made difficult by unusually low ambient temperatures at Danville. This presented some problems in the pelletization of the feed and resulted in a pellet feed containing a large proportion of fines. The strength of mixture K2 pellets was lower than that of mixture K3 pellets. Because pellet strength was a problem, KVS, in preparation for production runs, conducted the laboratory scale pelletization tests reported in Section 4.1.2.4.

The mixture K2 kiln run was conducted on the 17th and 18th of January. Kiln operating conditions were the same as those in the preceding run (2 rpm, slope of 3/8 in./ft, and oil burner rate 5 to 6 gph). The feed rate was 130 lb/hr.

The instrumentation provided for this run was the same as on the previous run except that the thermocouple at Port I was damaged and temperatures at this location could not be determined. The temperature profiles on the kiln are shown in Figures 8 and 9. Rate of product discharge, determined by weighing, is also plotted on these diagrams. Kiln residence time was about 1-1/2 hr. The residence time in the kiln appeared to be excessive and higher feed (and product) rates would have resulted in better conversions. Average product conversion to sulfide was 95.5%, while in Port I it was 98.4%. At the kiln discharge, all carbon disappeared from the pellets, whereas in Port I samples, about 25% of the original carbon was still retained. Table VII shows analytical data for the solids, while Table VIII shows gas analyses. Some oxidation of the pellets in the hot kiln zone probably occurred due to the lack of protection by the reducing gases liberated by carbon gasification. Excess oxygen was present since the oil burner used air atomization and the rates of oil combustion gas to reaction gases is higher in the small-scale pilot-plant kiln. The changes which occurred between Port I and kiln discharge indicate that gas diffusion into the pellets might have taken place.

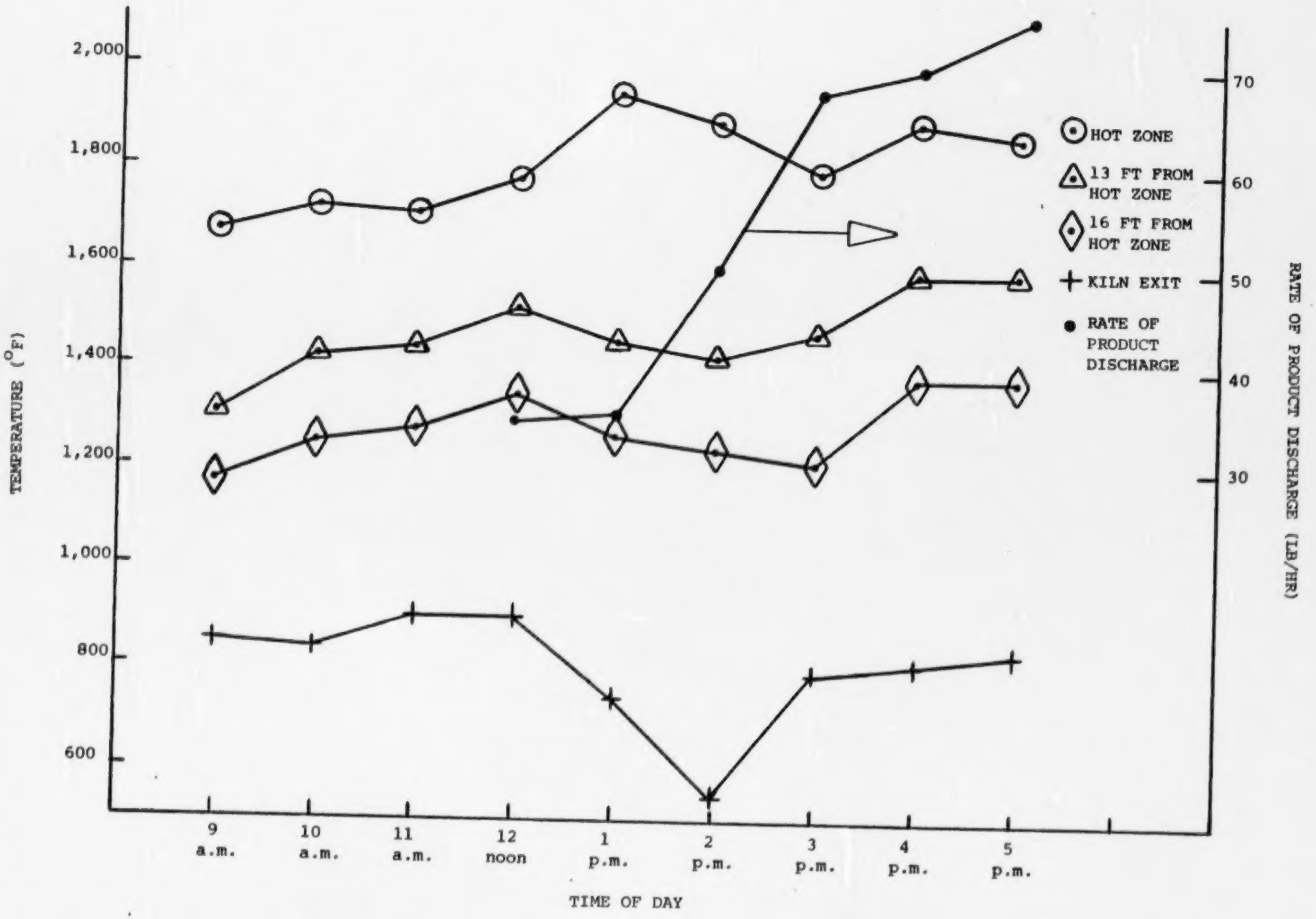

Figure 8.- Temperature profiles and rate of product discharge, mixture K2, 1/17/78.

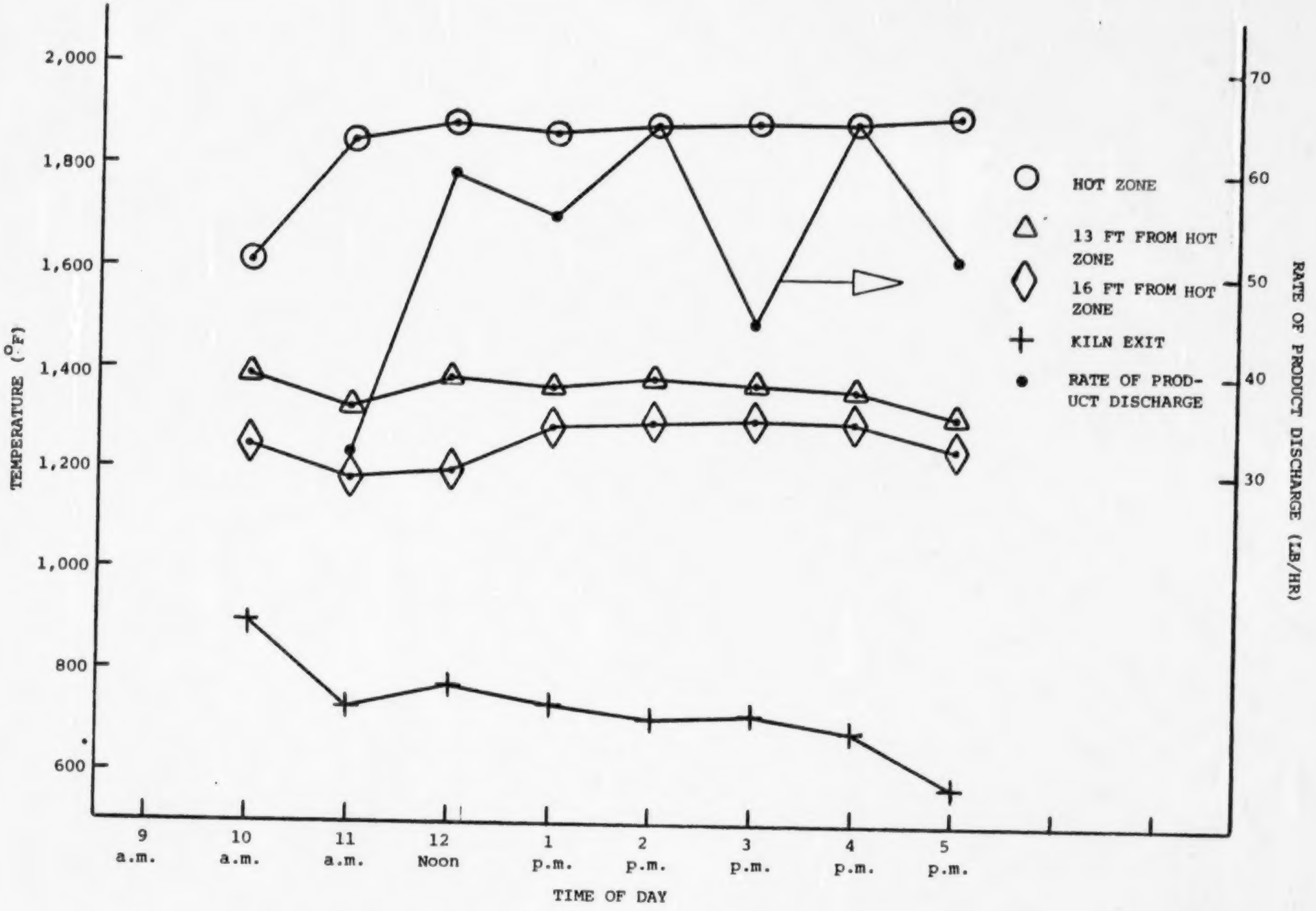

Figure 9.- Temperature profiles and rate of discharge, mixture K2, 1/18/78.

TABLE VII.- SUMMARY OF ANALYSES OF KILN SOLIDS
(17, 18, 19 JAN 1978)

Mixture	Sample Description	Date Sample Taken	Time Sample Taken (p.m.)	CaS (wt %)	$CaSO_3$ (wt %)	$CaSO_4$ (wt %)	$CaCO_3$ (wt %)	CaO (wt %)	Free Carbon (wt %)	Al_2O_3 (wt %)	FeO (wt %)	MgO (wt %)	SiO_2 (wt %)
K2	KD	1-17-78	12:00	39.82	0.89	3.42	0.54	32.76	0.0	-	-	-	-
K2	KD	1-17-78	2:00	39.71	0.24	1.46	0.36	32.65	0.0	-	-	-	-
K2	KD	1-17-78	4:00	34.40	0	3.78	1.90	36.79	0.06	-	-	-	-
K2	KD	1-18-78	1:00	34.16	0.12	3.48	1.20	37.63	0.02	-	-	-	-
K2	KD	1-18-78	3:00	34.53	0	2.08	0.62	35.91	0.0	-	-	-	-
K2	KD	1-18-78	5:00	39.84	0	1.92	0.81	30.77	0.02	4.05	3.04	0.92	11.80
K3	KD	1-19-78	12:00	35.40	0.12	3.75	0.36	33.85	0.01	-	-	-	-
K3	KD	1-19-78	2:00	39.89	0	1.81	0.33	32.47	0.01	-	-	-	-
K3	KD	1-19-78	4:00	36.26	0.12	1.25	1.37	33.63	0.0	-	-	-	-
K3	KD	1-19-78	6:00	35.17	0	1.06	1.32	36.00	0.0	3.86	3.41	0.94	12.34
K2	Port 1	1-17-78	4:00	37.27	0	1.69	14.37	19.46	3.83	-	-	-	-
K2	Port 2	1-17-78	4:00	4.10	0	39.32	25.82	7.45	-	-	-	-	-
K2	Port 3	1-17-78	4:00	0.25	0	45.11	34.61	0.0	-	-	-	-	-
K2	Port 1	1-18-78	5:00	29.61	0.12	8.35	23.44	15.08	4.54	2.94	2.82	0.76	8.88
K2	Port 2	1-18-78	5:00	0.22	0	44.87	26.08	5.33	-	2.07	1.86	0.53	3.16
K2	Port 3	1-18-78	5:00	0.12	0	42.91	25.83	3.29	-	1.99	1.88	0.50	6.71
K3	Port 1	1-19-78	2:00	16.64	0	26.39	27.91	10.63	4.31	-	-	-	-
K3	Port 2	1-19-78	2:00	0.20	0	46.33	26.73	5.05	-	-	-	-	-
K3	Port 3	1-19-78	2:00	0	0	44.13	27.29	3.96	-	-	-	-	-
K3	Port 1	1-19-78	6:00	24.43	0	15.23	19.06	17.85	3.32	2.80	2.65	0.87	8.12
K3	Port 2	1-19-78	6:00	0.34	0	46.00	21.44	7.70	7.81	1.66	1.73	0.47	6.73
K3	Port 3	1-19-78	6:00	0	0	42.85	27.88	3.84	-	1.86	1.69	0.50	2.77

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TABLE VIII.- GAS ANALYSES FROM KVS KILN (17, 18, AND 19 JANUARY 1978)

Date (Jan, 1978)	Time of Day	H_2S (mol %)	*O_2 (mol %)	N_2 (mol %)	*O_2 (mol %)	SO_2 (ppm)
17	1335	0.29	0.68	79.6	0.77	81
17	1400	0.30	0.63	64.0	0.72	
17	1538	0.32	0.72	63.8	0.86	
17	1602	0.05	0.98	65.8		
17	1656	0.05	0.71	67.6		
18	1030	ND	0.87	78.7		
18	1056				0.88	
18	1305				0.98	1240
18	1311	0.10	0.90		0.87	
18	1336				0.88	
18	1400	0.10	0.77	82.1		735
18	1426	0.21	0.71	77.9		
18	1454				0.86	
18	1510	0.39	0.67	77.2		
18	1530				0.81	
18	1546					406
18	1550	0.40	0.60	72.9	0.76	
18	1611					475
18	1617	0.32	0.63	74.8		
18	1655	0.32	0.67	73.1		
19	1109	0.23	0.75			
19	1140				0.88	
19	1145					130
19	1150	0.40	0.76			

*Oxygen was taken by two different instruments as a consistency check.

ND - not detected

TABLE VIII.- GAS ANALYSES FROM KVS KILN
(17, 18, AND 19 JANUARY 1978) (Contd.)

Date (Jan, 1978)	Time of Day	H_2S (mol %)	*O_2 (mol %)	N_2 (mol %)	*O_2 (mol %)	SO_2 (ppm)
19	1222				1.06	
19	1225	0.10	0.73			
19	1300					182
19	1305	0.03	0.67	80.0		
19	1310				0.79	
19	1345				0.82	
19	1350	0.47	0.63	76.7		
19	1430	0.10	0.80	71.9		
19	1445				1.06	
19	1630	0.62	0.62	74.1		
19	1700					390
19	1710	0.41	0.74	79.2		
19	1740	0.18	0.61	57.7		
19	1800				1.06	
19	1815				1.00	
19	1845	0.59	0.93			

*Oxygen was taken by two different instruments as a consistency check

The ratio between the amount of oil burned and the feed coal was much larger than would be the case in a commercial size plant because of excessive heat loss from the experimental unit. Operation of the kiln under stabilized conditions should allow better process conditions using increased ratios of feed coal to fuel oil. Higher ambient temperatures with lower heat losses would also help.

Very high conversion of $CaCO_3$ to CaO was observed in the kiln discharge, just as in the case of the K1 coal pellet mixture. The average carbon remaining in kiln discharge was 0.02% compared with 3.03% for the K1 pellets.

During the entire run with the K2 coal pellet mixture, a relatively high amount of fines was observed. It was impossible to determine, quantitatively, what the amount was because of the difficult access to the tail gas treatment of the unit. It appears that, in a continuous run, good process conditions could be established with mixture K2.

Verification that the Port I temperature (1,400° to 1,450° F) gave optimum results was not possible because the thermocouple at this location was missing.

4.1.3.4 Mixture K3 pellets.- The pellets for this run showed a lower amount of fines than the K2 pellets.

The run was conducted on January 19 with the same kiln conditions as on the previous day for K2 pellets. A somewhat lower rate of oil burning was achieved. The analytical instruments operated with acceptable accuracy, but the sampling line connecting the kiln discharge to the instruments had to be cleaned periodically. It became obvious that this line would have to be modified for the production run.

The average feed rate was some 20% higher than in the previous run (average product rate was 64 lb/hr compared to 53 lb/hr on the preceeding day), and once the kiln was lined out (by 1 p.m.) good process conditions were maintained for the rest of the day. The average reduction for the day was 97.2%, with half of the reducing reaction occurring in the hot zone between Port I and kiln discharge.

The effect of Port I temperature could not be evaluated because the thermocouple at this location was damaged. The temperature profile of the kiln was steady, and most of the reduction took place in the hot zone of the kiln.

The K3 mixture run was conducted at better kiln conditions than the K2 mixture. The temperature curves were steady, oil burning was at its lowest, and feed was at its highest.

The temperature profiles and the respective rates of product discharge are shown in Figure 10.

4.1.4 Bench Scale Tests

Bench scale tests were carried out to supplement the kiln reduction tests. The tests determined the effect of major process parameters while using only small amounts (5 g) of sludge. The bench scale tests were

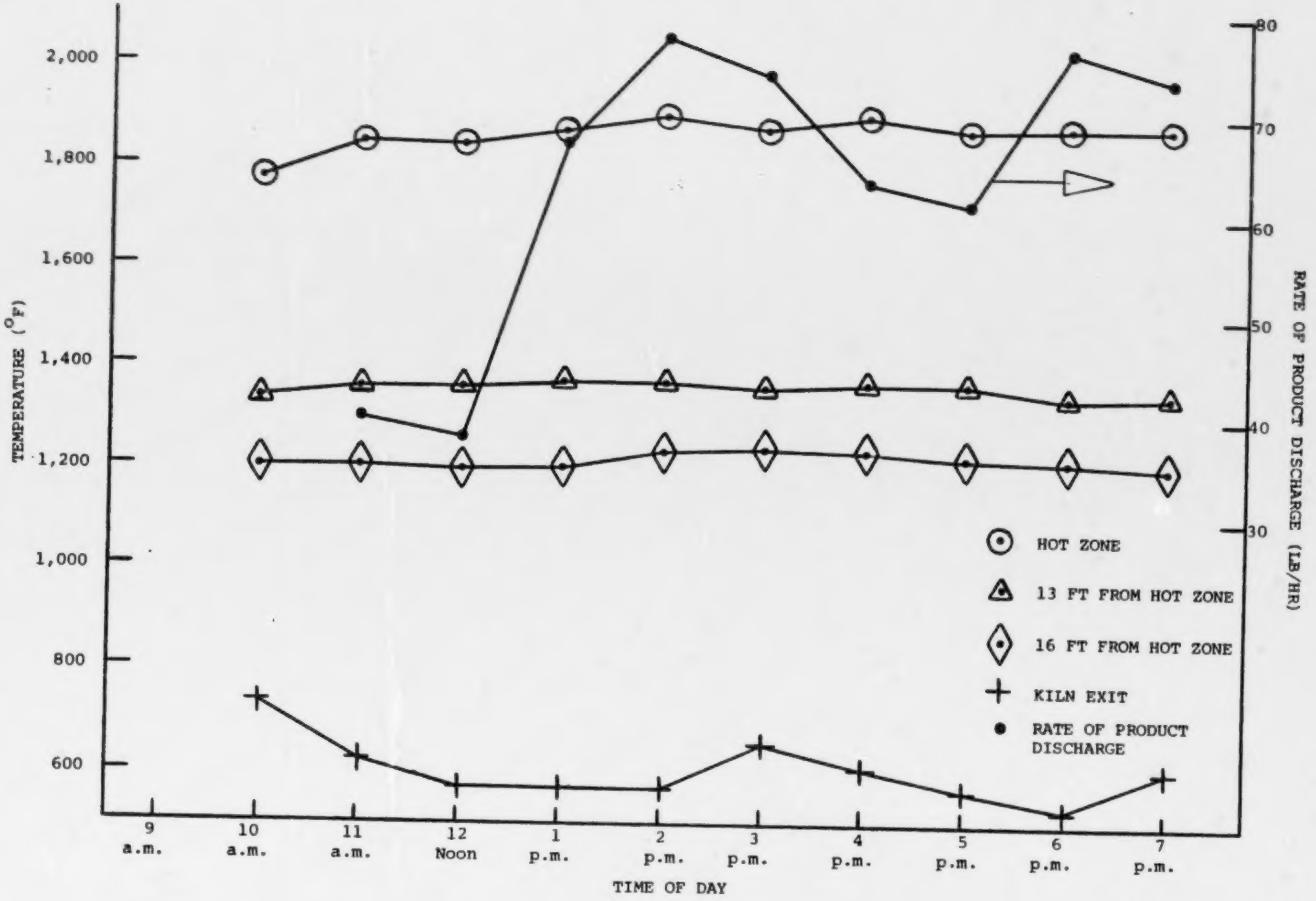

Figure 10.- Temperature profiles and rate of product discharge, mixture K3, 1/18/78.

advantageous since they produced a large amount of data under precisely controlled conditions within a relatively short time, and did it more economically when compared to a pilot size kiln. A program was established for studying the major variables, i.e., coal content in the feed pellets, particle size, type of coal, heatup rate, and reaction time.

4.1.4.1 Apparatus.- The reactor consisted of a 4-foot length of 1-inch diameter, 310 stainless-steel tubing heated by a Lindberg (Model 34357) three-zone furnace (Figure 11). A stream of nitrogen was introduced into the branch of the tee at one end of the reactor, and a 5-foot movable thermocouple was fitted through the run of the tee and made gas-tight. An Alundum boat was attached to the end of the thermocouple in a manner which allowed the boat to be positioned in the reactor by moving the thermocouple. The other end of the reactor was closed with a rubber stopper and, was connected to a tar trap and a sparged gas scrubber (Figure 12). Offgases were scrubbed with H_2O_2 and $CdSO_4$ to determine SO_2 and sulfides, respectively.

4.1.4.2 Procedure.-

A. Preparation of sludge and coal - The Will County Sludge was obtained from Allis Chalmers after it had been concentrated to 90% solids. The sludge was dried overnight at ambient temperature under 30 inches of vacuum. The clumps were broken apart with a mortar and pestle and passed through a Tyler 100 mesh screen.

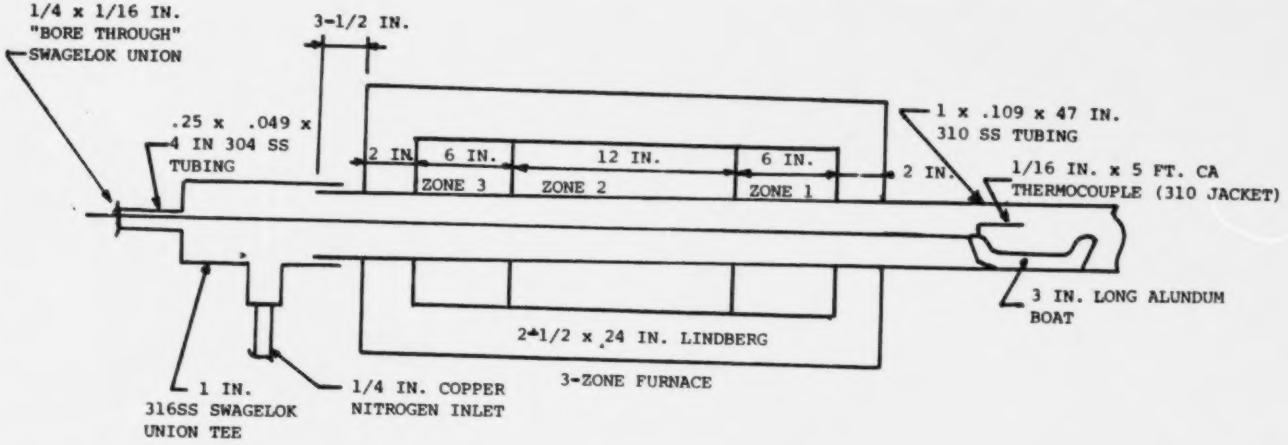
1/4 x 1/16 IN.
"BORE THROUGH"
SWAGELOK UNION
3-1/2 IN.
.25 x .049 x
4 IN 304 SS
TUBING
2 IN.
6 IN.
12 IN.
6 IN.
2 IN.
ZONE 3
ZONE 2
ZONE 1
1 x .109 x 47 IN.
310 SS TUBING
1/16 IN. x 5 FT. CA
THERMOCOUPLE (310 JACKET)
3 IN. LONG ALUNDUM
BOAT
2-1/2 x 24 IN. LINDBERG
3-ZONE FURNACE
1 IN.
316SS SWAGELOK
UNION TEE
1/4 IN. COPPER
NITROGEN INLET

Figure 11.- Furnace and reactor test setup.

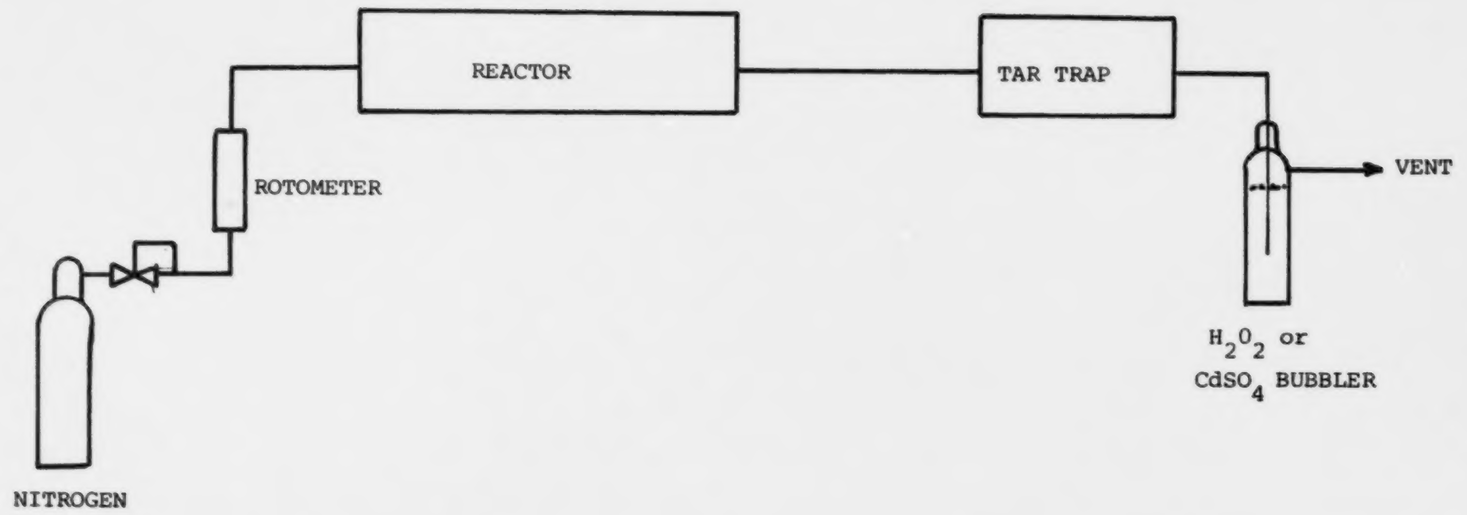
REACTOR
TAR TRAP
ROTOMETER
VENT
NITROGEN
H_2O_2 or
$CdSO_4$ BUBBLER

Figure 12.- Bench scale sludge reduction unit, schematic diagram.

Western Kentucky #9 coal was ground by Kennedy Van Saun to pass a Tyler 100 mesh screen.

B. Preparation of pellets - A mixture of the requisite amounts of coal and dry sludge (total 100 parts) was mixed with 4 parts of minus 200 mesh bentonite. Thirty parts of water were added to this mixture, and then enough additional water was used to form a workable paste. The paste was formed into 1/4 in. diameter balls, either by rolling it between the hands, or by rolling it in a stone mill jar until the balls formed. Both methods worked equally well in the laboratory, and neither formed balls as strong as those made at Kennedy Van Saun. The balls were allowed to dry overnight at room temperature, then for 1/2 hr at 300° F.

C. Typical run - Approximately five pellets were placed in the boat, which was positioned so that it was out of the heated zone of the reactor. The end of the reactor was closed, and a stream of N_2 (about 1 cu ft/hr) was established. The furnace was turned on and set at 1,000° F for Zone 1, 1,700° F for Zone 2, and 1,750° F for Zone 3. After 2 hours, the temperatures were stabilized, and the air had been displaced by nitrogen. The boat was pulled along the reactor by the thermocouple, so that the sample was heated along a predetermined profile. At the end of the desired total contact time, the boat was pushed to the cool end of the reactor and cooled for an hour. Then pellets were removed from the reactor, weighed, and analyzed.

D. Analysis of reduced pellets - The pellets were ground and dissolved in HCl under nitrogen. The gases developed were analyzed for sulfide and sulfite, and the soluble material was analyzed for sulfate. These values were reported in weight percent as their calcium salt. The acid-insoluble residue was analyzed for carbon by the standard method used for carbon analysis of coke.

4.1.4.3 Test program.-

A. Variation of pellet composition - The amount of coal in the pellet was varied from 0% to 35%, bentonite was held at 4% and the remainder of the pellet consisted dried sludge solids. This series of pellets was used to determine the optimum amount of coal required for complete reduction of the sludge.

To demonstrate the non-utility of volatile carbon in the coal (the carbon in the material volatilized from the coal under reaction conditions), a sample of coal was pyrolyzed under reaction conditions and the resultant char was used to make pellets.

B. Variation of contact time - To ascertain the effect of contact time on the degree of reduction, and to determine the best contact time for the reaction, pellets of the same batch were reduced for varying lengths of time.

C. Sulfur problems - Pyrolysis of coal volatilizes a fair amount of the sulfur in the coal. The sulfur-bearing components include H_2S, mercaptans, aromatic sulfur compounds, and thiophene. To reduce the amount of mercaptans and H_2S being evolved from the bench scale unit, lime was added to the pellets. Sulfur compounds are evolved from the coal before the $CaCO_3$ is calcined to lime. The added lime then captures the sulfur compounds.

To render the remaining sulfur into a form which is less toxic, air was introduced into the reactor downstream of the reaction zone, but at a point where the gases were at least 1,000° F. This technique oxidized all the reduced sulfur compounds to SO_2, which is a less toxic compound.

4.1.4.4 Results.-

A. General - The limestone stack gas scrubber sludge was received from Kennedy Van Saun Corporation after it had been concentrated to 90% solids. The analysis is given under Column A-2 in Table I. The Western Kentucky #9 coal used is >95% finer than USA series 100 mesh. This analysis is shown in Table II.

B. Experimental data - Twenty-one simulated kiln runs were made under two basic conditions. Table IX summarizes the results of these 21 runs. The first condition called for heating the sample to 1,700° F over 35 min. Figure 13 presents the average temperature profile for the 35-min heatup. The second scheme was to place the sample in the

TABLE IX.- KEL-S SLUDGE REDUCTION ANALYTICAL DATA

RUN:	1	2	3	4	5	6	7	8	9	10
Pellets (batch)	KVS-9	1	1	[a]Coal	5	4	1	6	1	1
Heatup time (min)	35	35	35	35	35	35	97	35	10	100
Contact time (min)	45	45	45	45	45	45	120	45	45	120
Analysis of product										
CaS (%)	49.87	44.22	47.24	--	54.88	49.04	44.68	43.29	44.31	47.93
$CaSO_3$ (%)	0.07	0.06	0.75	--	1.80	0.84	0.90	1.05	1.35	1.35
$CaSO_4$ (%)	1.80	0.14	1.52	--	1.04	1.11	1.14	1.32	1.17	0.49
C (%)	7.84	8.51	--	--	10.00	7.60	8.75	7.50	7.76	8.55
Weight loss (%)	44.3	47.8	50.4	40.5	49.7	43.9	49.7	50.0	49.1	55.9
Selectivity	98.0	99.7	97.4	--	96.4	97.8	97.5	97.0	96.8	97.8
Yield	95.8	99.7	97.4	--	96.4	97.8	87.5	86.2	87.8	82.4
Sulfur balance (frac)	0.98	1.01	1.05	--	1.07	1.00	0.90	0.89	0.91	0.84
SO_2 evolved (%)	0.03									
H_2S evolved (%)			0.09	0.94			0.0	0.05	0.04	0.04

---

[a] Run as powder

TABLE IX.- KEL-S SLUDGE REDUCTION ANALYTICAL DATA (Contd.)

RUN:	11	12	13	14	15	16	17	18	19	20	21
Pellets (batch)	7	8	9	7	7	10	11	11	11	11	11
Heatup time (min)	35	35	35	35	35	35	4	2	2	2	2
Contact time (min)	45	45	45	45	45	45	45	15	30	10	5
Analysis of product											
CaS (%)	28.09	48.48	42.36	32.26	42.17	1.21	33.93	36.06	35.19	26.47	10.41
$CaSO_3$ (%)	6.75	1.8	0.75	16.20	1.65	4.2	5.25	4.50	7.08	16.66	3.20
$CaSO_4$ (%)	12.53	0.78	0.49	5.47	15.02	55.18	3.01	14.10	7.09	24.12	36.55
C (%)	0.09	1.18	0.11	0	0	--	0.16	0.15	0.08	1.68	4.78
Weight loss (%)	42.6	97.0	98.3	47.2	42.0	25.5	47.0	43.7	47.2	37.7	26.7
Selectivity	72.7	48.6	45.2	71.9	82.6	3.7	80.4	78.0	81.4	53.7	32.8
Yield	54.2	88.7	80.3	57.3	82.8	3.4	60.5	68.3	62.5	55.5	25.6
Sulfur balance (frac)	0.75	0.91	0.82	0.80	1.00	0.94	0.91	0.88	0.77	1.03	0.78

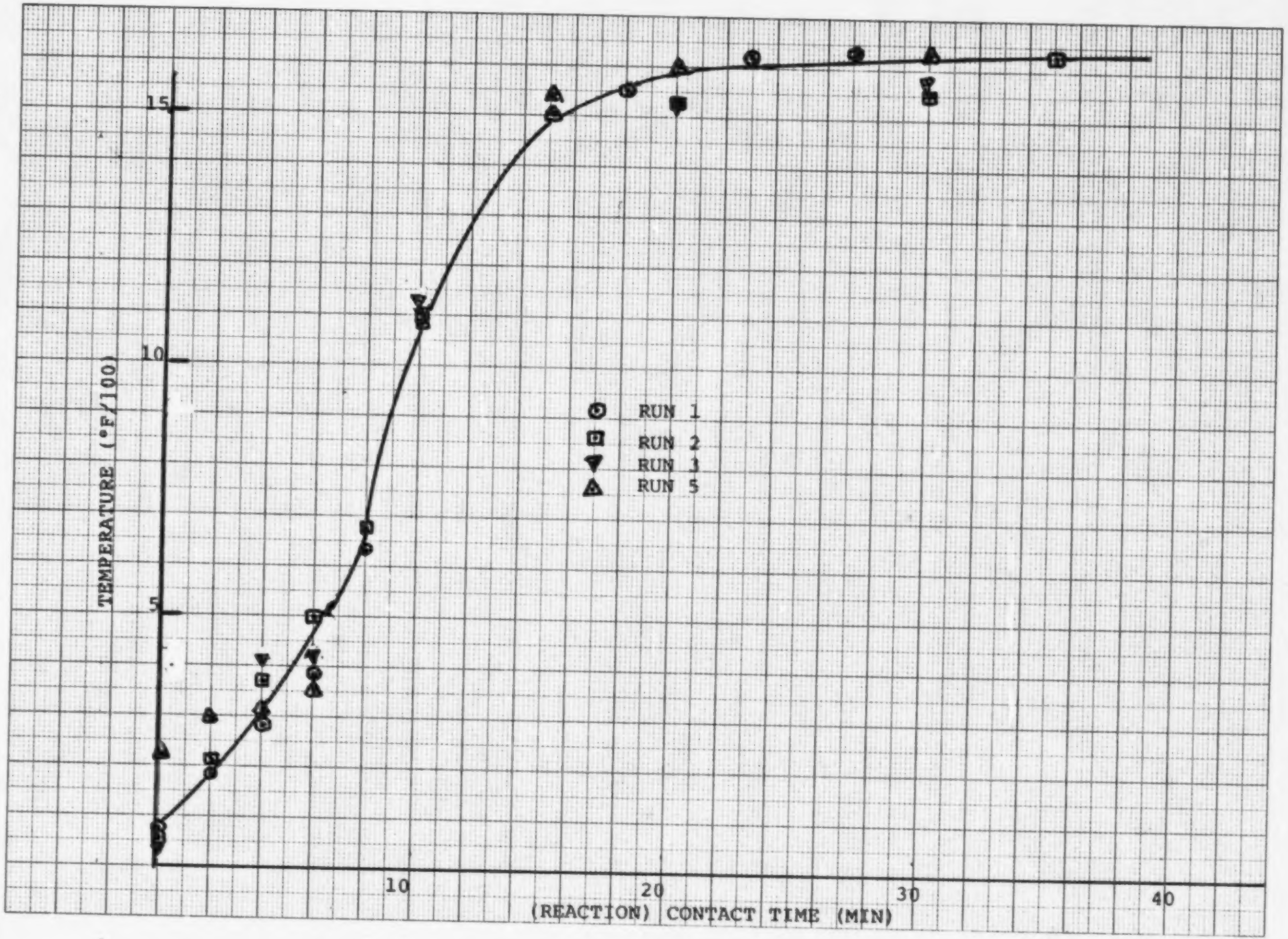

Figure 13.- Kel-S sludge reduction temperature during reaction.

1,700° F zone of the reactor as rapidly as possible.

C. Variation of coal content - The coal content of the pellets was varied from 0% to 35%. The conversion of calcium sulfate to calcium sulfide increased from about 3% to 99% as the percentage of coal increased. (See Figure 14.)

D. Variation of run time - A series of runs were made in which the contact time was the only variable. Pellets containing equal amounts coal were heated as rapidly as possible to 1,700° F and held there. The reaction was then quenched by placing the pellets in the cool end of the reactor. The conversion of $CaSO_4$ to CaS, and the coal conversion are shown in Figure 15. Figure 16 shows the amount of $CaSO_4$ found in the pellets as a function of contact time, compared against the $CaSO_4$ level in pellets run by Allis Chalmers in 1974. These two figures show that the optimum contact time for the rapidly heated samples was 15 min. For samples which were heated over 35 min to reaction temperature of 1,750° F, 30 min was optimum. An investigation of the literature[1] showed that 1,470° to 1,650° F was optimum to reduce calcium sulfate on ignition with carbon. At about 1,400° F, the volatile matter in the coal is evolved so rapidly, that a portion of the carbon in

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[1] Gmelins Handbuch der anorganischen Chemie, system number 28, Calcium, Part B3, p. 703(1961); P. P. Budmkov, M. I. Nekirch, Khim. Promyshlennost, 402(1955)

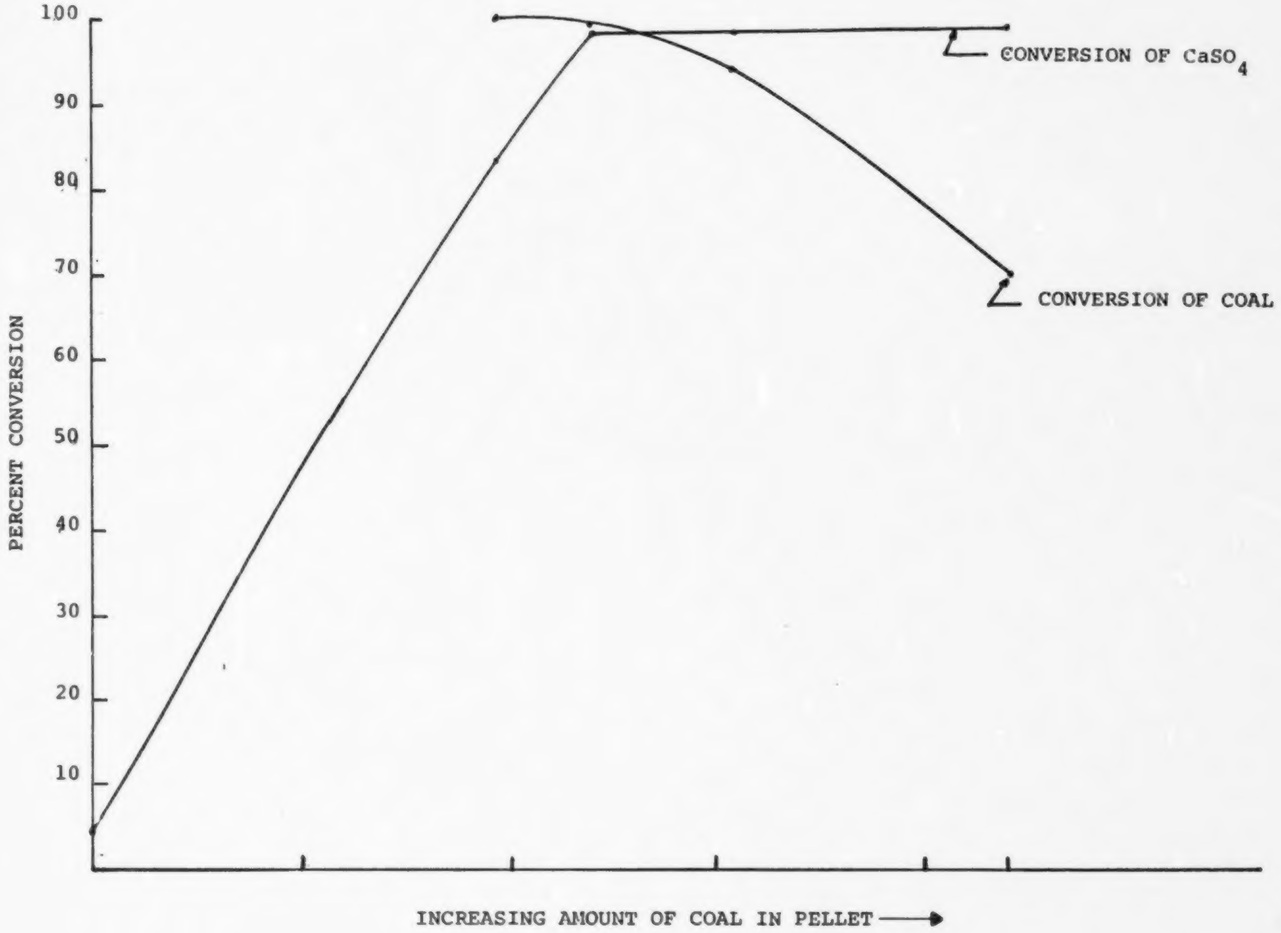

Figure 14.- Kel-S conversion of sludge by varying amounts of coal.

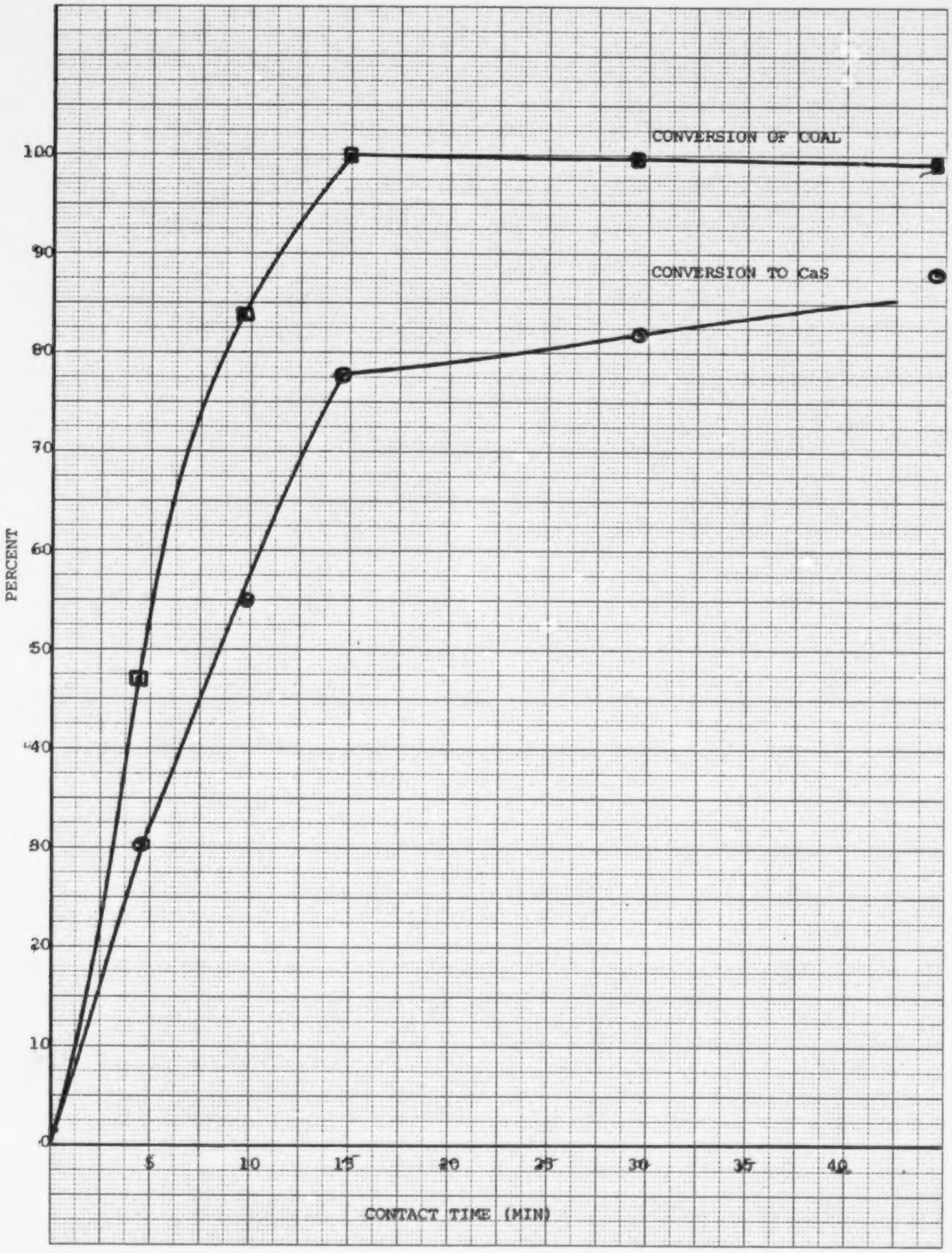

Figure 15.- Reaction of sludge with Western Kentucky #9 Coal, at 1710° F with 2 minute heatup.

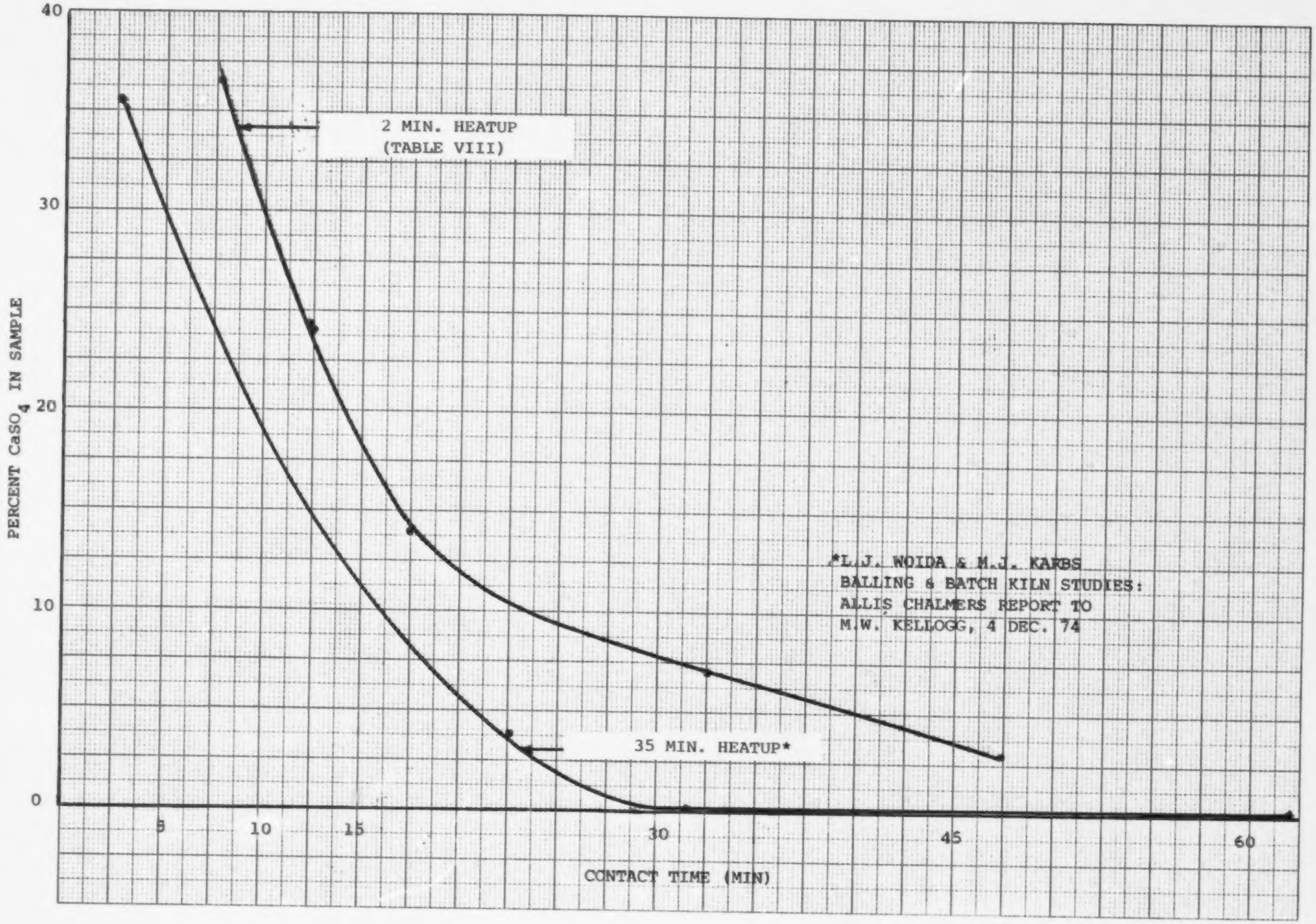

Figure 16.- $CaSO_4$ Level in Kel-S pellets during the reduction of $CaSO_4$.

the coal escapes unreacted. Long reaction times can lead to sulfur losses by reoxidizing CaS to $CaSO_3$ ($CaSO_3$ is unstable above 1,200° F).

E. Reduction with coal char - Char from coal which had been "devolatilized", i.e., pyrolyzed at 1,700° F, was used in one run to compare with the results obtained by using coal. Run 2 with coal gave 100% conversion to CaS. Run 5 with char (with an equivalent amount of carbon to Run 2) gave 96.4% conversion to CaS. These results are essentially the same.

F. Air lance - The coal evolved H_2S as well as other sulfur-bearing volatiles on pyrolysis. Addition of air to the reactor (Run 7) below the reaction zone oxidized all the H_2S and mercaptans to SO_2.

G. Addition of lime - Addition of lime to the pellet reduced the amount of H_2S evolved by half (cf. Runs 3 and 8). The change was from 0.09% to 0.05% H_2S by weight of the pellet.

Coal can evolve many other sulfur-bearing compounds besides H_2S and mercaptans. The most volatile of these are thiophene and its derivatives. Addition of lime will trap the H_2S; however, oxidation is necessary during bench scale operations to render the other S-bearing compounds innocuous.

4.2 CARBONATION TESTS

Bench scale tests were conducted to define operating conditions for the carbonation and flotation steps. Carbonation tests were carried out at Kellogg's R&D Center, Houston, Texas; the flotation tests were done at Denver Equipment Company's facilities, Denver, Colorado. Feed material needed for the flotation tests was produced in the carbonation experiments.

The primary variables needing definition in the carbonation step were particle size of reduced sludge, kinetics of CO_2 sludge reaction, excess CO_2 required, and maximum H_2S in reactor effluent gas. Flotation tests were designed to find maximum calcium carbonate separation from coal ash and other impurities at an acceptable (~80%) recovery efficiency of calcium carbonate.

4.2.1 Apparatus/Procedure

4.2.1.1 General procedures.-

A. Apparatus - A diagram of the bench scale unit used for the carbonation of kiln reduced sludge is shown in Figure 17.

B. Equipment -

- o Autoclave Engineers - 1 gal autoclave with magnadrive stirrer.
- o Grove Regulator Company - Back pressure regulator.

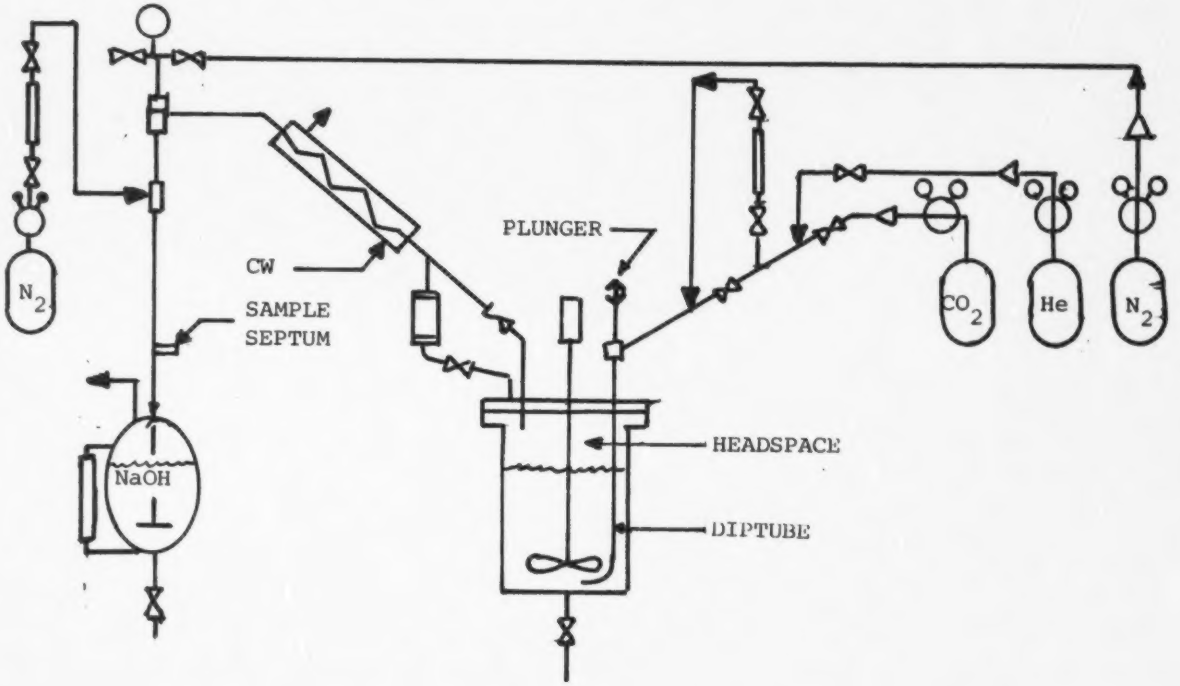
N$_2$
NaOH
CW
SAMPLE SEPTUM
PLUNGER
HEADSPACE
DIPTUBE
CO$_2$
He
N$_2$

Figure 17.- Kel-S carbonation, bench scale unit, final design.

- Hewlett Packard Chromatograph Model 5750 with T.C. Detector. Column: Deactigel 60/80, Applied Science Lab, Inc, 1/8 in. OD by 3 ft length, operated at 80° C, helium flow rate 30 cm^3/min.

C. Chemicals -

- CO_2 - Linde Commercial Grade
- He - Liquid Air, Inc. Prepurified
- N_2 - Liquid Air, Inc.
- NaOH - Matheson Coleman and Bell

D. Experimental procedure - The system was first tested for leaks at 60 psig using helium. About half the amount of distilled water necessary for the slurry was added through a fitting in the head of the autoclave. The stirrer was started and helium was allowed to flow through the sparger tube. A weighed amount of dry, ground and screened (-140 mesh), kiln-reduced sludge was poured into the autoclave, followed by the remaining water to produce the desired slurry concentration (usually 7.3 wt % solids in 3 liters of slurry).

The autoclave was heated to the required temperature by balancing the heat input of its furnace against the cooling water coil inside the unit. A helium flow was maintained through the sparger to keep it from plugging. After the system reached stable temperature, the helium was stopped and, at the same time, CO_2 flow was begun at the required flow rate. Samples of offgas were taken at the sample septum, just upstream of the scrubber about every 3 minutes during the run. The samples were analyzed by gas chromatography to determine mole % N_2, H_2S, and CO_2. The effluent flow rate was calculated from the measured nitrogen concentration. (Nitrogen was bled into the flow of offgas at a constant rate.)

Occasionally plugging was indicated by a temporary decrease in the CO_2 rate, and it was necessary to clear the sparger using the plunger built into it.

The CO_2 feed was continued at a constant rate until the concentration of H_2S in the offgas was below 0.5%. Then the autoclave was sealed off with valves and cooled to below 100° F using the cooling coil. The contents were purged into a 1-gallon jar through the bottom valve while stirring was continued. It was then rinsed once with 400 ml of distilled water, and the rinse water was added to the product container.

The autoclave was opened for inspection and, in those cases where the general procedure was used, it was found to be essentially clean. Samples of the kiln-reduced sludge starting material, and the carbonated products were submitted for analysis by wet chemical methods.

4.2.1.2 Deviations from general procedure.-

A. Air flotation test sample preparation (sent to Denver Equipment) - In these initial sample preparation runs, a sparger was not used for CO_2 addition, nor was the flow of offgas measured. Offgas samples were taken to determine the H_2S and CO_2 concentrations.

B. Interrupted runs - In one case, the CO_2 addition was stopped after the H_2S concentration in the offgas had decreased from its maximum value.

In another case, the CO_2 addition was stopped after a calculated stoichiometric volume had been added to the autoclave (sufficient CO_2 to react with the total CaO and CaS in the slurry).

In both the above experiments, H_2S was purged from the system with helium, then CO_2 feed was started again. The amount of H_2S produced was measured.

C. Non-sludge runs - In several experiments, U.S.P. CaS, with and without $CaCO_3$, was used instead of reduced sludge. Also, in one test, water was placed in the autoclave to determine the holdup time between the start of CO_2 feed and its appearance at the sample point.

4.2.2 Program

Table X lists the conditions and maximum H_2S% measured for the test program. Runs 1-3 were used to prepare samples for flotation tests and to determine characteristics of the reaction. Low H_2S

TABLE X.- CARBONATION REACTIONS

Run No.	Slurry % Solids	 Total Volume liters	T °F	P PSIG	CO_2 Feed Rate l/min	H_2S Max %	Comments
1	15	2	260	60	1.0	74.5	Product analyzed. Used for initial flotation studies.
2	7.3	2	250	60	1.0	46.4	Product used for initial flotation studies.
3	25	2.4	250	60	1.0	55.9	Product used for initial flotation studies.
4	15	2	250	60	0.54	57.5	1 mole CO_2 introduced before run initiated.
5	15	2	250	60	0.54	15.6	Autoclave found to contain sludge when opened after run.
6	7.3	3	250	60	0.54	81.5	First attempt with dip tube, severe plugging. Flow rate not constant.
7	7.3	3	250	60	0.54	44.4	Dip tube plugged. Switched to overhead.
8	7.3	2	250	60	0.54	61.3	Dip tube fitted with 10μ frit - plugged before CO_2 introduced. Switched to overhead.

TABLE X.- CARBONATION REACTIONS (Contd.)

Run No.	Slurry % Solids	Slurry Total Volume liters	T °F	P PSIG	CO_2 Feed Rate 1/min	H_2S Max %	Comments
9	7.3	3	250	60	0.54	44.5	Dip tube with 1/32" hole used - plugged before CO_2 introduced - switched to overhead.
10	7.3	3	250	60	1.0	39	Filter fitted to gas inlet line. Dip tube plugged before CO_2 introduced - switched to overhead.
11	7.3	3	250	60	0.54	96.9	Dip tube with plunger used. Run interrupted when H_2S scrubber plugged.
12	7.3	3	250	60	1.0	93.9	Poor slurry formation. Solid present in reactor after run.
13	7.3	3	250	60	0.54	97.8	Reactor found to be clean after run.
14	7.3	3	250	60	1.0	88.6	Flow meter fitted to exit line.
15	7.3	3	250	60	1.5	83.8	Flow meter found to be unreliable due to water condensation.

TABLE X.- CARBONATION REACTIONS (Contd.)

Run No.	Slurry % Solids	 Total Volume liters	T °F	P PSIG	CO_2 Feed Rate 1/min	H_2S Max %	Comments
16	7.3	2	250	60	1.0	92.1	N_2 dilution flow monitoring system established.
17	7.3	3	250	60	1.0	88.7	CO_2 flow interrupted after 1.6 moles/mole of Ca compound delivered. Reaction 99.9% complete.
18	7.3	3	275	74	1.5	83.8	
19	7.3	3	250	60	1.0	90.7	Synthetic sludge containing CaS and $CaCO_3$ only.
20	7.3	3	250	60	1.5	97.9	Dip tube modified to final configuration.
21	7.3	3	200	42	1.5	97.9	
22	7.3	3	200	42	1.5	98.2	Pure CaS
23	7.3	3	250	60	1.5	--	Pure CaO
24	7.3	3	150	35	1.5	96.8	
25	7.3	3	200	42	1.5	97.4	Larger particle size
26	7.3	3	200	24	1.5	93.9	Low P_{CO_2}

TABLE X.- CARBONATION REACTIONS (Contd.)

Run No.	Slurry % Solids	Slurry Total Volume liters	T °F	P PSIG	CO_2 Feed Rate 1/min	H_2S Max %	Comments
27	7.3	3	250	60	1.5	98.1	Stoichiometric amount of CO_2 introduced. Reaction 98.5% complete.
28	7.3	3	250	60	1.5	99.3	Pure CaS

concentrations in the outlet stream in these runs indicated a need for better gas-liquid mixing.

Attempts were made to introduce the CO_2 into the slurry through a dip tube. Serious problems were encountered with plugging in these tubes, even with inert gas flowing through the tube. A modification of the dip tube was adopted that incorporated a plunger which allowed plugs to be removed from the tube as they formed. The dip tube was later modified to provide optimum gas-liquid contact by extending the dip tube to a point directly beneath the stirrer impeller.

After optimum reaction conditions were established, the effect of sludge particle size was examined (Run 25). A reaction was performed on a sludge consisting of particles between 12 and 140 mesh and compared with a reaction in which the sludge was less than 140 mesh.

The effects of reaction temperature and CO_2 partial pressure were studied. Reactions were also performed with pure chemicals which are known to be components of the sludge to determine the characteristics of the reactions of these components under our conditions.

4.2.3 Results

4.2.3.1 Analysis of reduced sludge and carbonated product.- Analyses were performed on the reduced sludge from the kiln runs at KVS. This material was also re-analyzed after grinding and sieving to less than 140 mesh.

REDUCED SLUDGE FROM KILN RUNS

	Before Grinding (wt%)	After Grinding (wt%)
CaS	37.91	38.56
CaO	24.86	23.70
$CaCO_3$	2.18	2.14
$CaSO_3$	0.30	5.70
$CaSO_4$	0.51	2.68
Free C	7.66	7.22
Acid Insolubles	3.33	2.16
Total	76.75	82.16

Increases in $CaSO_3$ and $CaSO_4$ after grinding were due to air oxidation during grinding.

CARBONATED PRODUCT

	Run #1	Run #6
CaS	1.01	0.74
$CaSO_3$	3.00	3.45
$CaSO_4$	4.24	3.43
$CaCO_3$	66.50	70.27

The analyzed carbonated products are from early runs in which CO_2 was injected into the headspace. Even with this inefficient method of CO_2 mixing, carbonation was 98% complete.

4.2.3.2 Concentration of H_2S and CO_2 in effluent.-

Since the effluent from the carbonation step of the process is used as a feed for a Claus plant, high concentrations of H_2S in this stream are desirable. Preliminary experiments in glass containers at low pressure had indicated that high concentrations were obtainable from the carbonation reaction. However, the early autoclave reactions, which were performed by injecting the gas into the headspace, resulted in <50% H_2S concentrations. Addition of a dip tube to the reactor, allowing gas injection below the surface of the slurry, resulted in an increase in the H_2S offgas concentration (85%-95%) and a marked shortening of the reaction time (Figure 18).

The dependence of H_2S concentration in the effluent on the CO_2 flow rate through this first dip tube is shown in Figure 19. It can be seen that the maximum H_2S percent in the effluent decreases with increasing flow rate when this straight dip tube is used. This type of dependence is indicative of inefficient gas-liquid mixing and led to the design of a dip tube extending to a point directly below the stirrer. This final design change resulted in H_2S offgas concentrations of ~98% when the CO_2 flow rate was 1,500 cm^3/min, a great improvement over the 84% H_2S obtained with the straight dip tube. Figure 20 shows a comparison of the results obtained with the two dip tubes.

In all these runs, CO_2 was the only other gas involved in the reaction, $\%CO_2 = 100 - \%H_2S$.

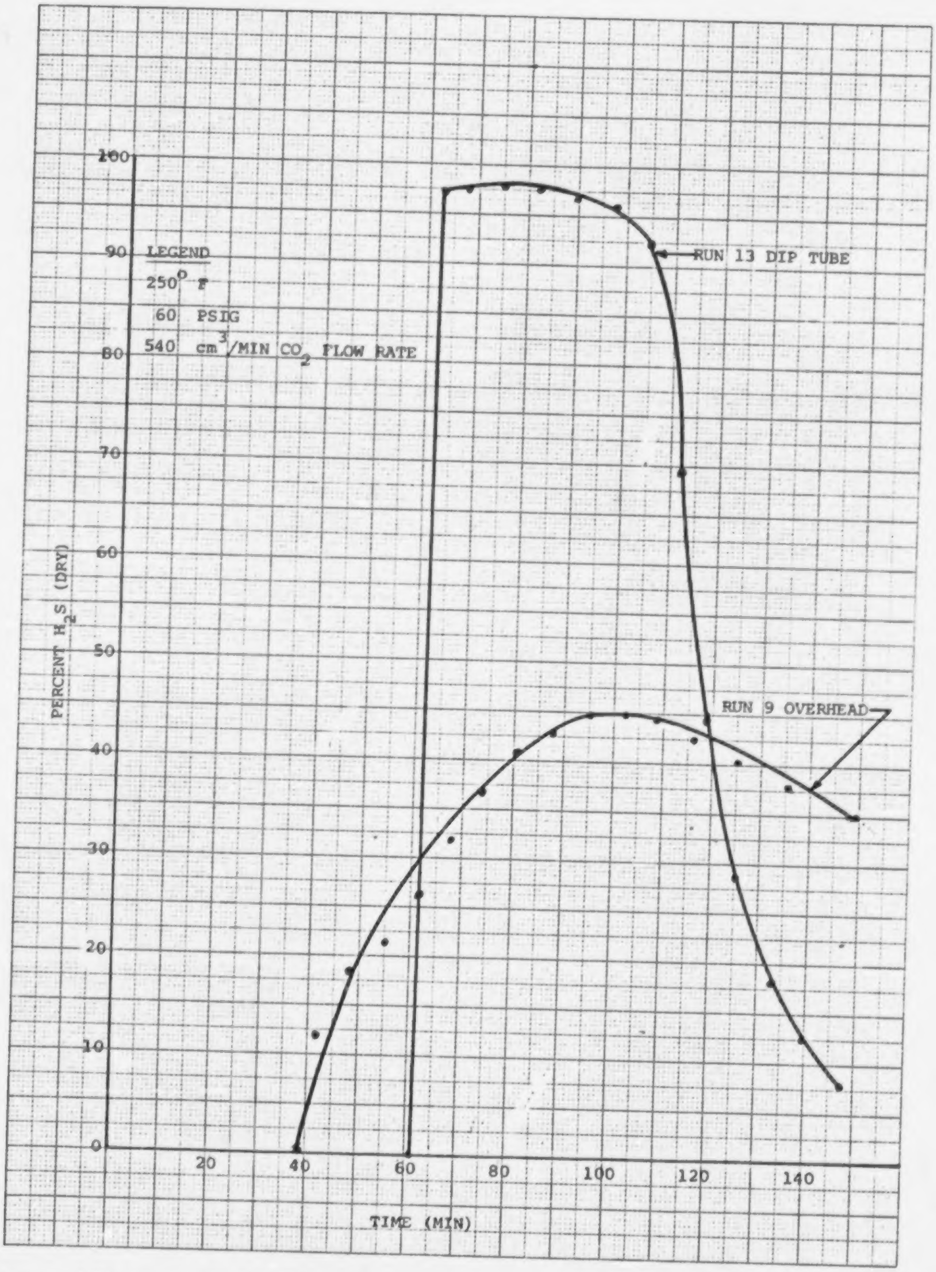

Figure 18.- Carbonation of reduced sludge, percent H_2S in effluent vs time - Dependence on method of CO_2 introduction.

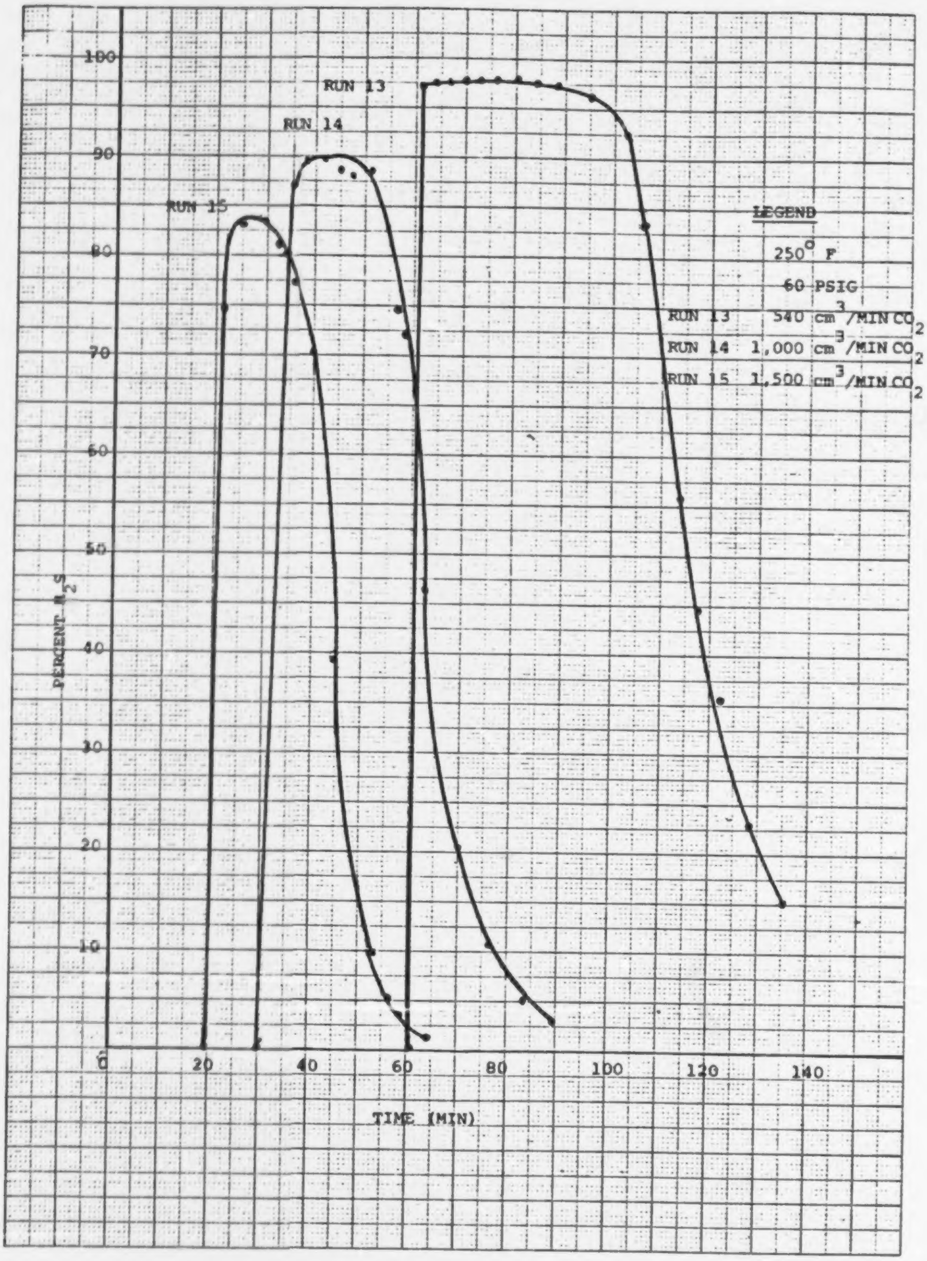

Figure 19.- Carbonation of reduced sludge, percent H_2S in effluent vs time - Dependence on CO_2 flow rate.

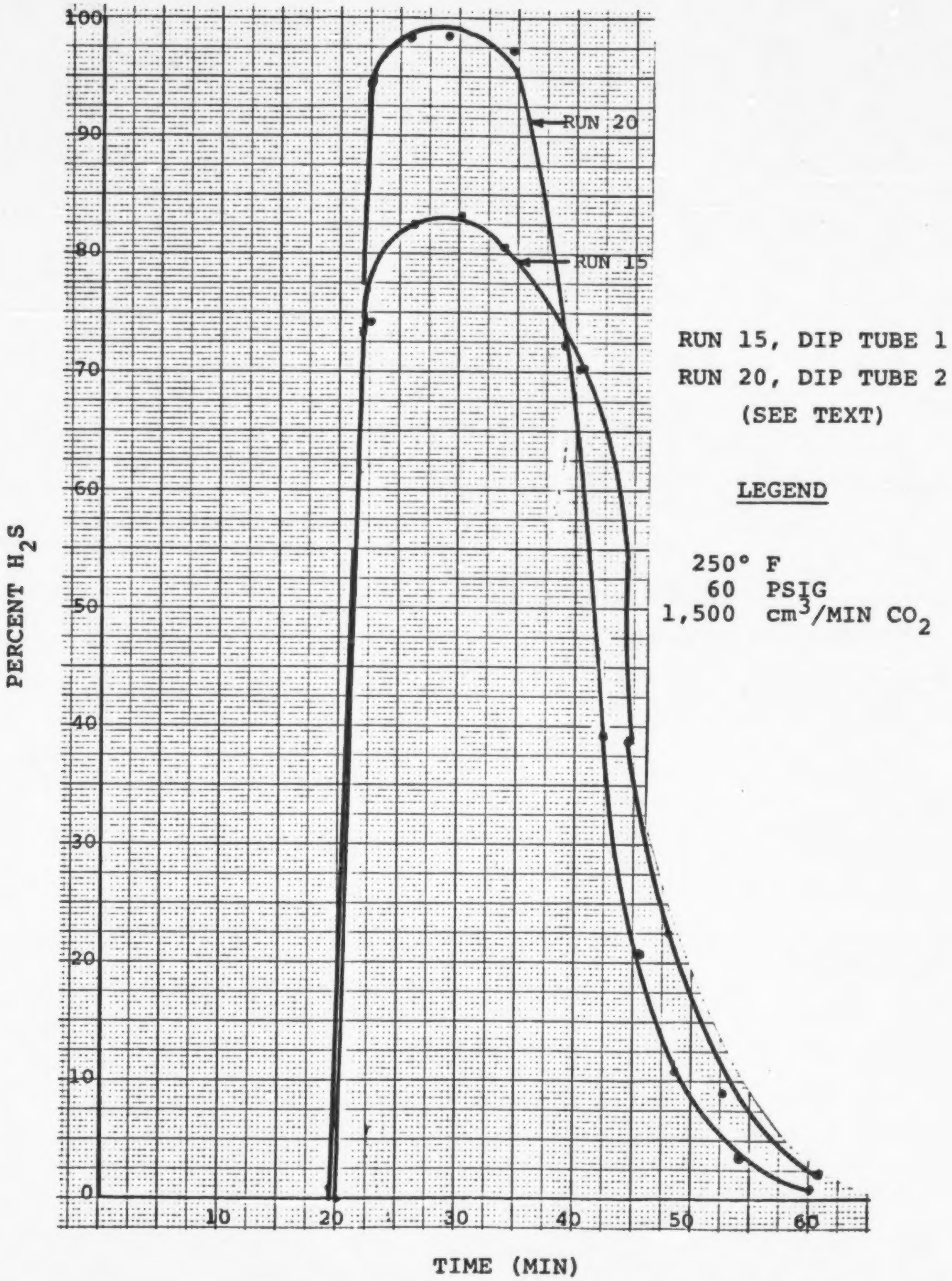

Figure 20.- Carbonation of reduced sludge, percent H_2S in effluent vs time - Dependence on dip tube design.

4.2.3.3 Results of interrupted runs.- Two runs were performed in which the flow of CO_2 was interrupted after a measured amount of CO_2 had been supplied to the reactor. The gas in the reactor was then swept out with an inert gas and CO_2 was reintroduced to determine if any sulfide was still present. The reactor was purged with He after 71.15 liters of CO_2 (3.18 mol) was added to the reactor which already contained 1.17 mol of CaS and 0.93 mol of CaO in the sludge (51% excess CO_2). Only an additional 4.7×10^{-2} liters (2.09×10^{-3} mol) of H_2S were found in the offgas when CO_2 was again introduced. Thus, the reaction had gone to 99.98% of completion.

A similar experiment was conducted by adding a stoichiometric amount of CO_2 to the slurry in the reactor. When CO_2 was later reintroduced after purging with He, only 1.5% of the total H_2S that could have been produced was found in the offgas (98.5% completion).

These experiments lead to the conclusion that the reaction is fast and irreversible. The reaction times, as measured in our data, are actually only the total time needed to purge the system of the H_2S produced. Carbon dioxide that exceeds the stoichiometric amount necessary to convert the CaO and CaS to the carbonate serves only as a purge gas.

4.2.3.4 Effect of particle size.- Two runs were performed under identical reaction conditions (200° F, 1,500 cm^3/min CO_2 flow rate, and 42 psig) with sludge in one case ground to less than 140 mesh, and in the other case, ground to between 12 and 140 mesh. The results are presented in Figure 21. The ordinate of the figures will now be changed to cc/min. of H_2S or CO_2, since the percent H_2S in the offgas does not directly indicate the speed or extent of reaction because the total offgas flow rate is variable through the runs. The maximum percent H_2S obtained (which gives its suitability for Claus plant feed) is given in Table X.

The small differences in the H_2S curve are probably due mainly to aging of the large particle size sludge. This solid had not been protected from the atmosphere before the slurry was prepared. Note that the maximum H_2S concentration for runs 21 and 25 is about the same as given in Table X.

4.2.3.5 Effect of temperature.- Runs were performed at 150°, 200°, and 250° F under constant CO_2 partial pressure and identical CO_2 flow rates to determine the effect of temperature on the reaction. Figure 22 shows the results of these runs expressed as H_2S flow rate versus time.

The only systematic difference in the curves is the increase in delay time as the reaction temperature is decreased. This fact can be explained by the increasing solubility of H_2S in water as the temperature decreases. The variation in the height and time of the maxima of the curves does not appear to be systematic, but is probably due to experimental errors. There is no apparent kinetic effect of temperature on the reaction.

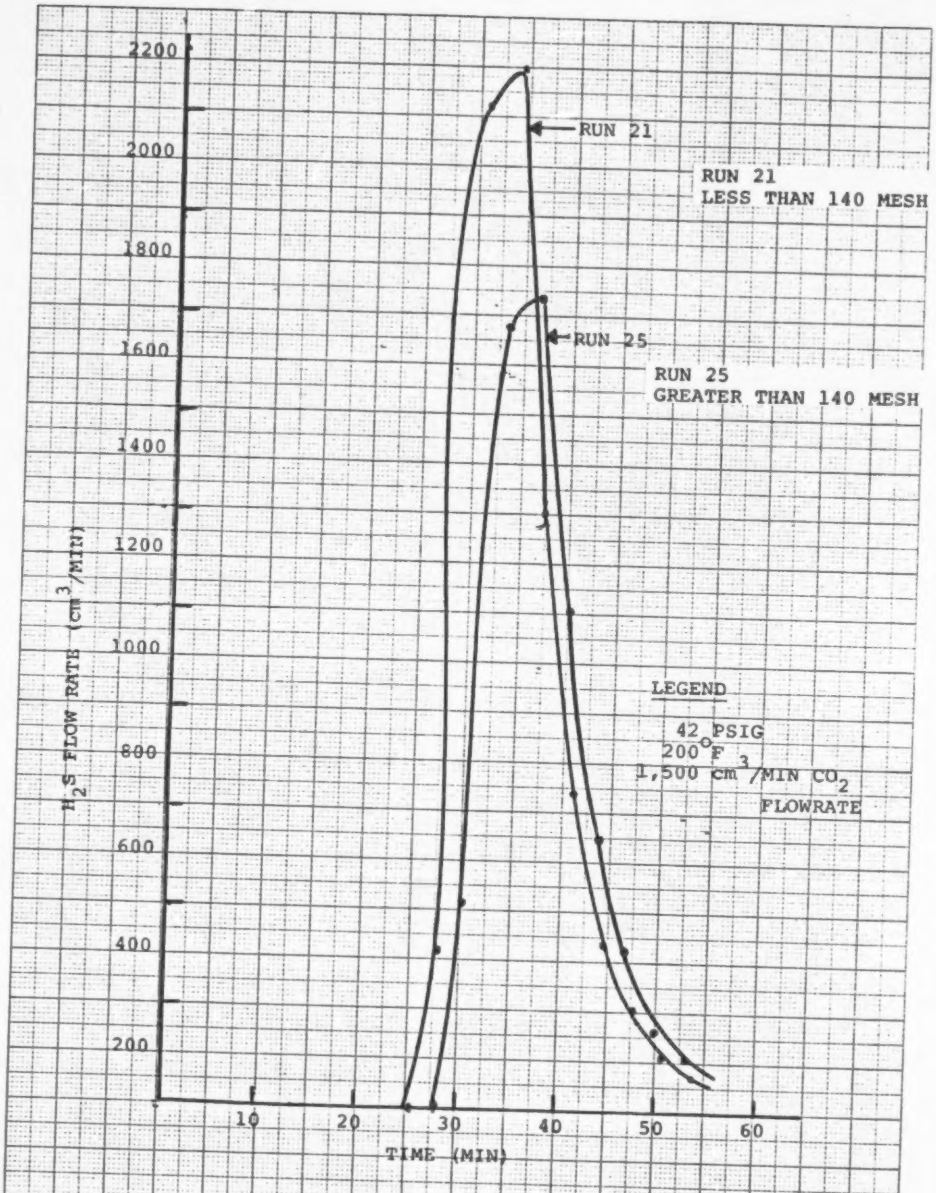

Figure 21.- Carbonation of reduced sludge, H_2S flow rate vs time - Dependence on particle size.

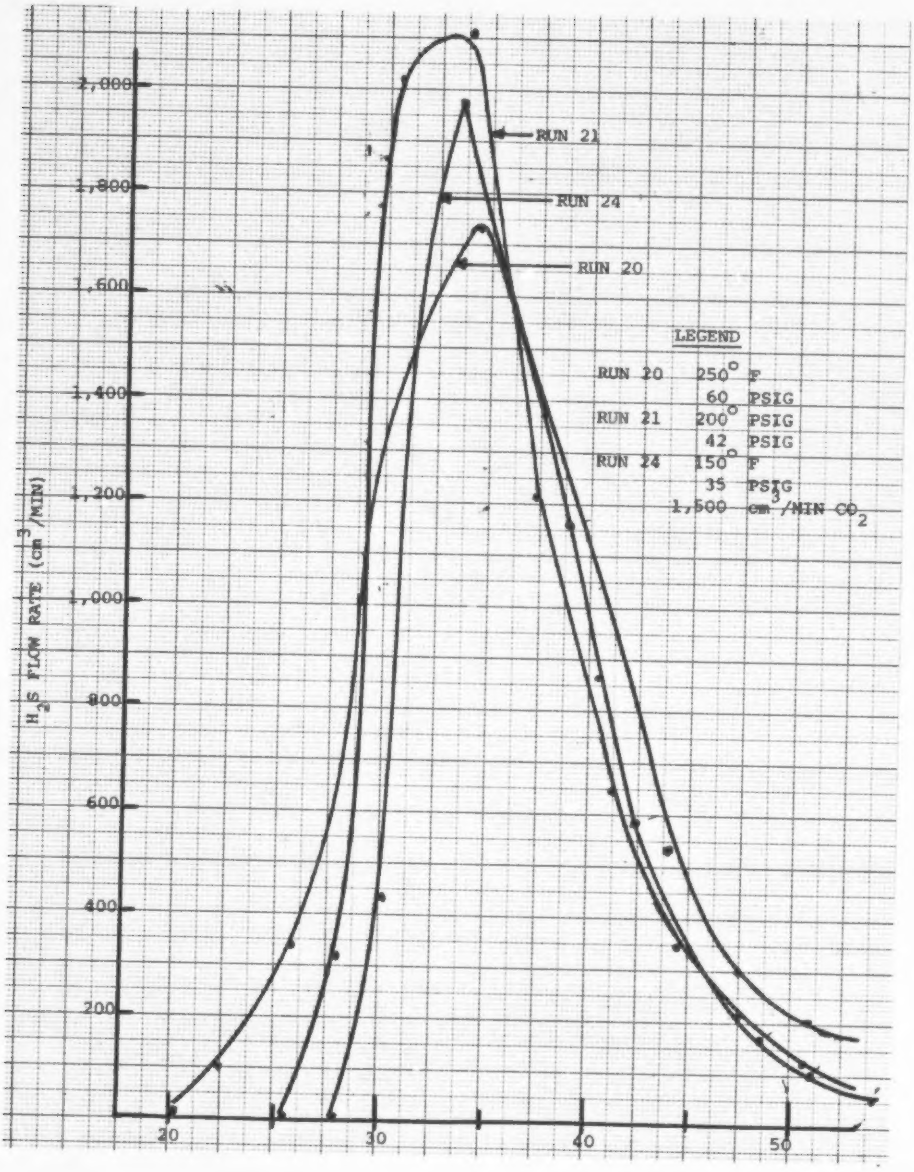

Figure 22.- Carbonation of reduced sludge, H_2S flow rate vs time - Dependence on reaction temperature.

4.2.3.6 Effect of pressure.- Two runs were performed at 200° F and with a 1,500 cm^3/min CO_2 feed rate. Only their total pressure (and, therefore, CO_2 partial pressures) differed. The results of these runs are shown in Figure 23. The differences in these runs also appear to reflect the difference in solubility of H_2S under varying pressure.

4.2.3.7 Pure component runs.- In all pure component runs, an initial period was observed in which no CO_2 or H_2S was detected and no pressure change occurred. This initial period was due, at least in part, to the reaction:

$$CaO + CO_2 \rightarrow CaCO_3.$$

In this reaction, CO_2 is absorbed by the solid CaO and the pressure remains constant. This type of delay has been confirmed by performing a run on a slurry of pure CaO.

There was also a delay in the equipment itself. For example, in a run in which the slurry was replaced by pure water or a $CaCO_3$ slurry, there was a delay between the initial injection time and the time at which CO_2 was first observed in the exit gas. The delay was caused by the volume of unoccupied space in the reactor and exit lines.

In those reactions where the exit gas flow rate could be measured, the maximum H_2S flow rate out of the reactor was actually higher than the CO_2 inlet flow rate. In the pure component runs in which a pure CaS slurry was used, the flow rate measured on the exit

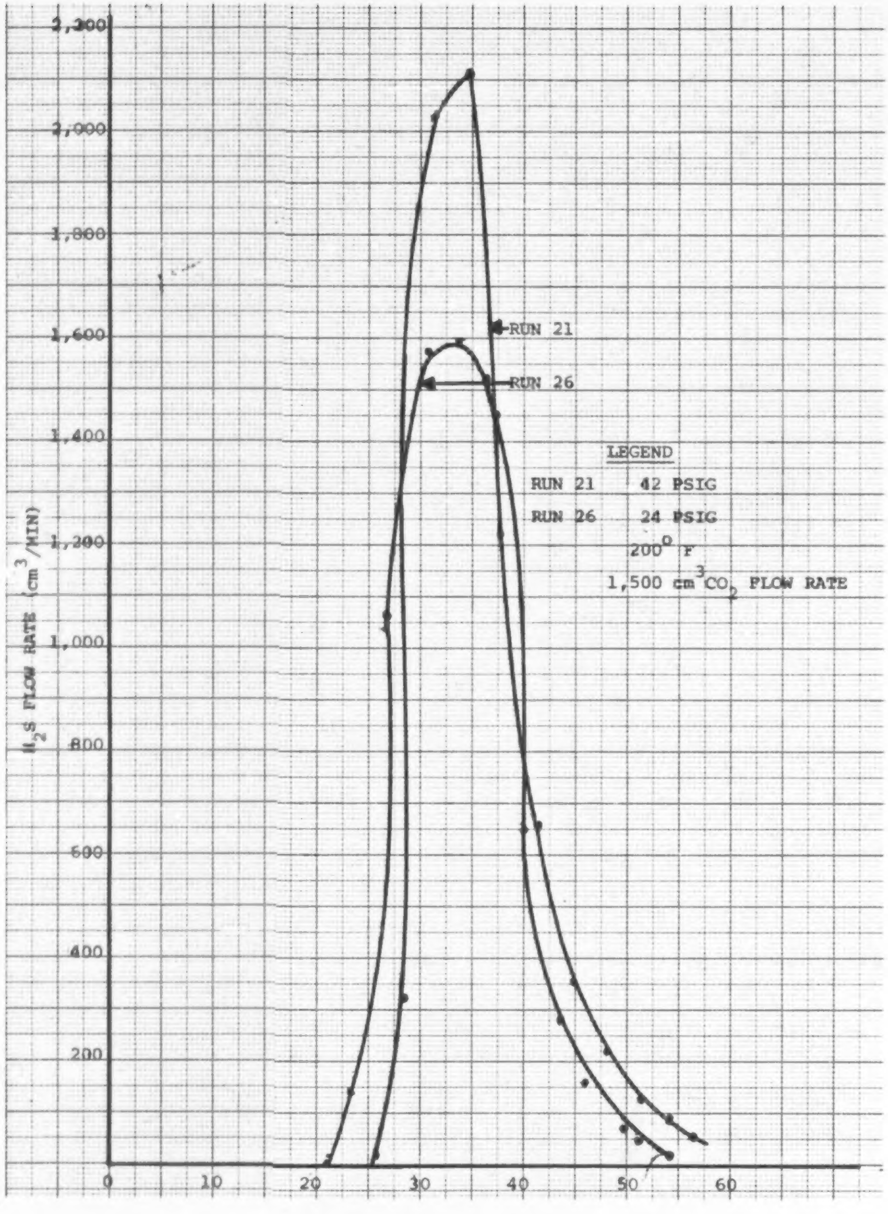

Figure 23.- Carbonation of reduced sludge, H_2S flow rate vs time - Dependence on pressure.

stream was almost twice the inlet CO_2 flow rate. In addition, with a pure CaS slurry, there was also a delay which cannot be accounted for by the equipment. These facts led to the conclusion that the reaction actually occurred in two steps. The first,

$$2CaS + CO_2 + H_2O \rightarrow CaCO_3 + Ca(HS)_2$$

involved no gas evolution and would lead to the type of delay mentioned above. The second reaction,

$$Ca(HS)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2S$$

accounted for the increased exit gas flow rate, since 1 mole of CO_2 absorbed in this step released 2 moles of H_2S gas. The overall reaction, however, was the same as was the stoichiometry:

$$CaS + CO_2 + H_2O \rightarrow CaCO_3 + H_2S$$

4.2.4 Data Analysis

Results from four typical runs were analyzed. The analyses considered both the reduced sludge and pure CaS samples under the different reaction conditions shown below:

REACTION CONDITIONS OF
FOUR TYPICAL CARBONATION RUNS

Test Run No.	Batch Reactor Charge[a]	Reaction Conditions[b]
20	Reduced Sludge	60 psig & 250° F
21	Reduced Sludge	42 psig & 200° F
22	Pure CaS	42 psig & 200° F
28	Pure CaS	60 psig & 250° F

---

[a] 220 g solids in 3-liter slurry

[b] CO_2 feed rate 1,500 cm/min (atm) continous

Experimental results of the four runs were converted into rates of CO_2 absorption and H_2S evolution (in millimoles/min) observed at the sample port. These rates were plotted as a function of time (min), and they are shown in Figures 24 through 27. The data points had been obtained in about 3-min intervals. Peaks of the H_2S evolution curves were obtained, not from the actual measurements, but from extrapolations with previous slopes.

4.2.4.1 Time lag.- A large time lag between the point of actual reaction and the point of product sampling occurred as a result of the tubing connections and accessories such as the condenser unit. Besides the effect of time lag, back mixing of the product gas also occurred to some extent in the volume of space in the system, and this prevented an accurate accounting of the reaction kinetics.

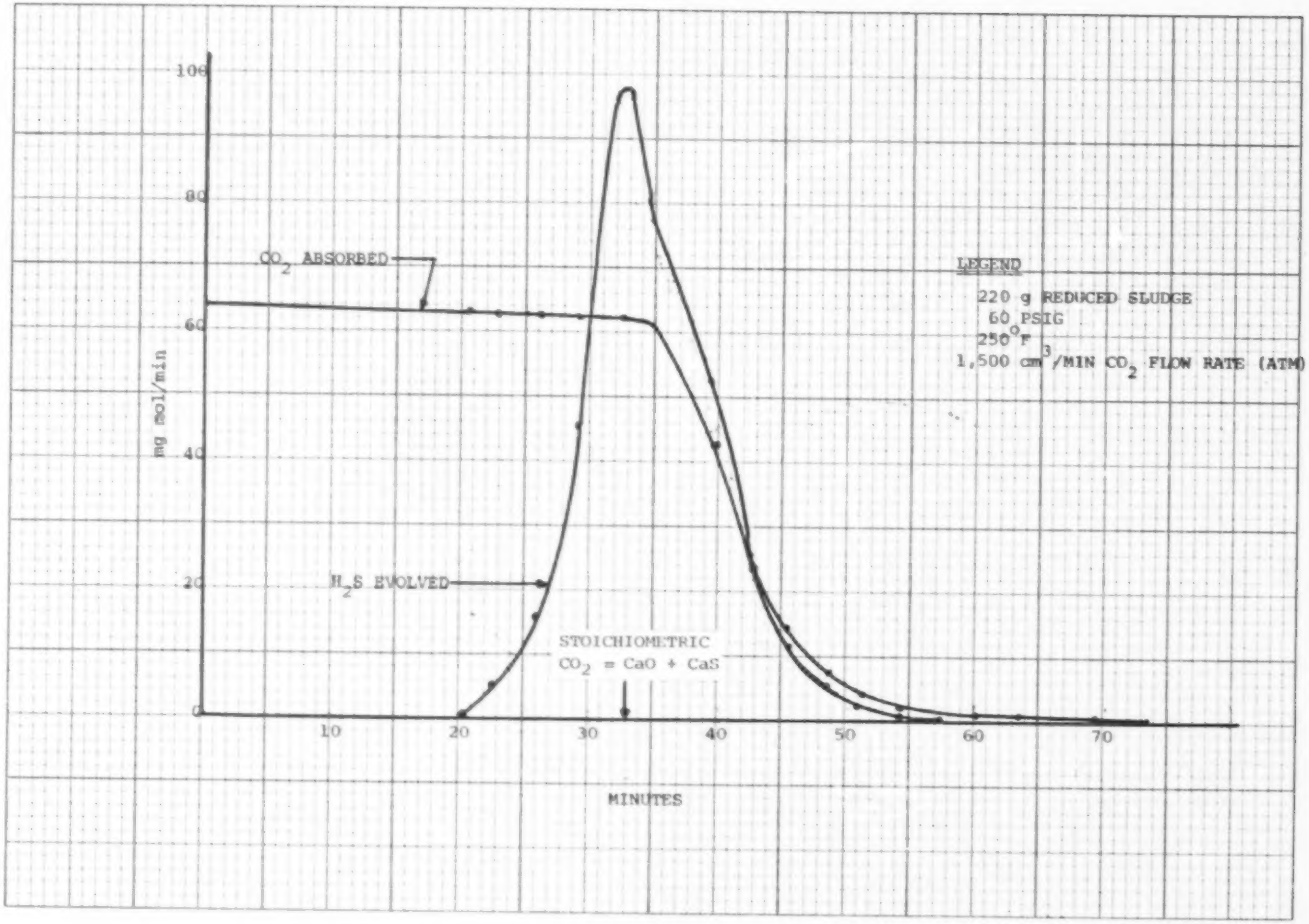

Figure 24.- Carbonation run 20, 3 liter slurry (7.3% solids).

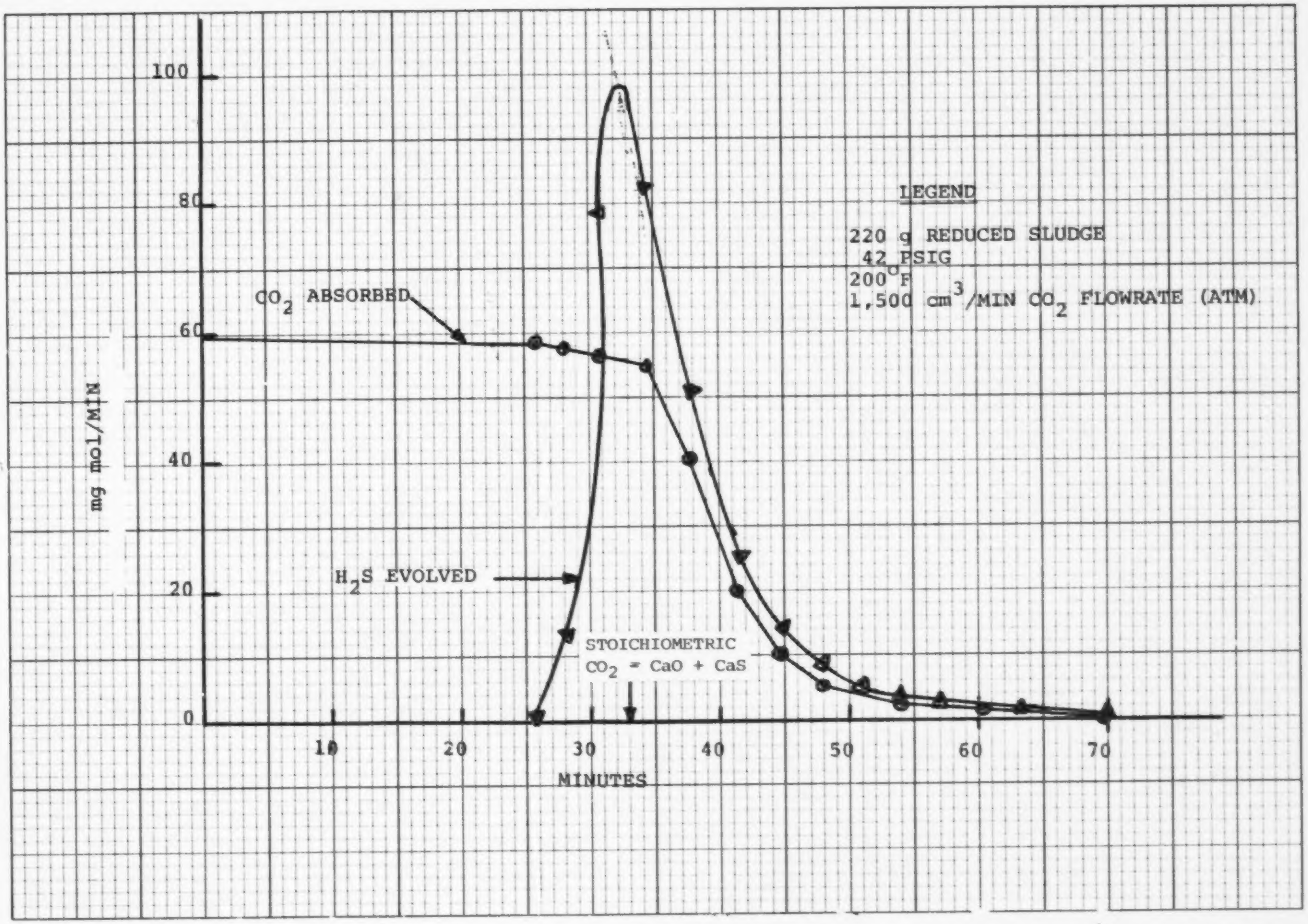

Figure 25.- Carbonation run 21, 3 liter slurry (7.3% solids).

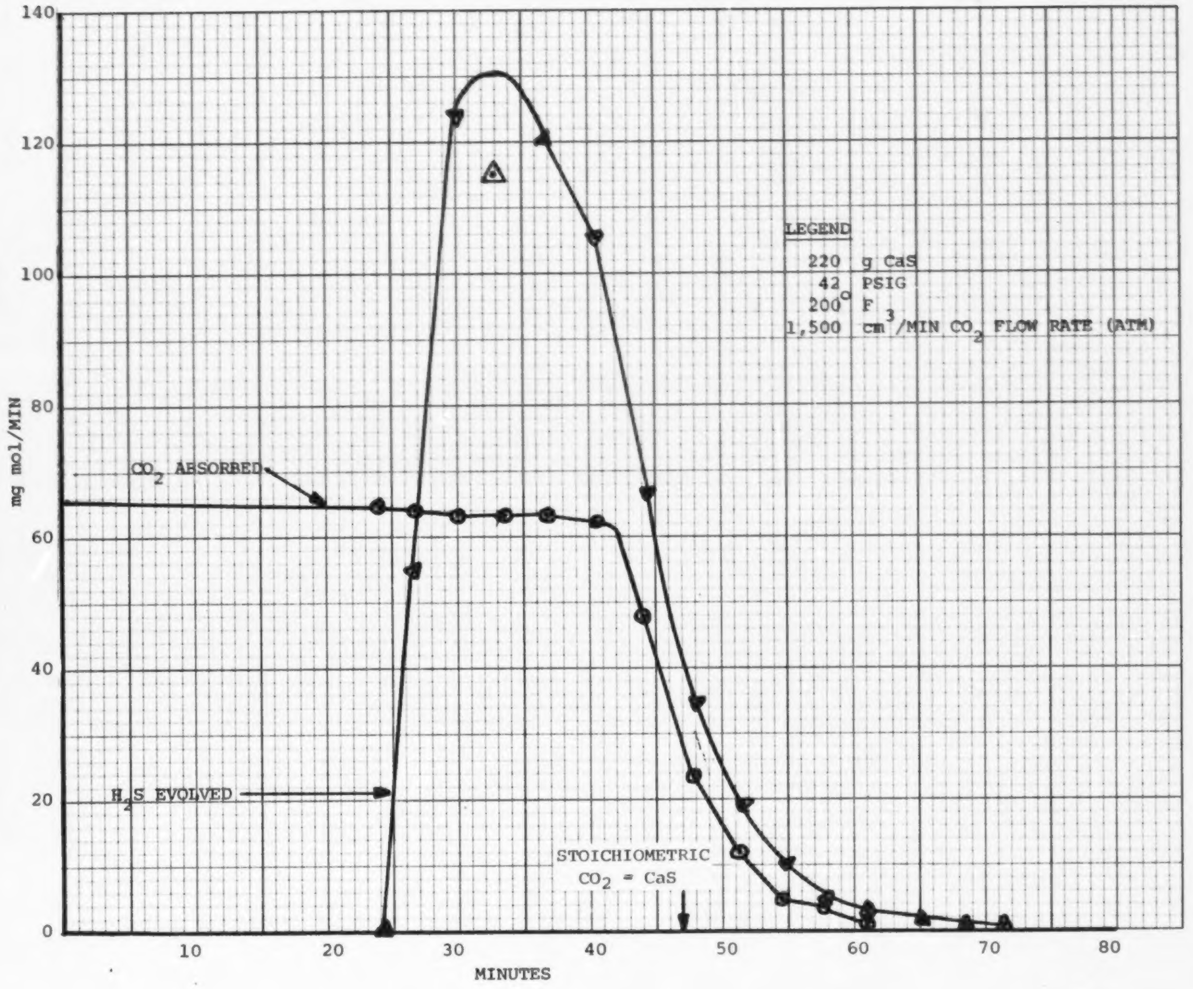

Figure 26.- Carbonation run 22, 3 liter slurry (7.3% solids).

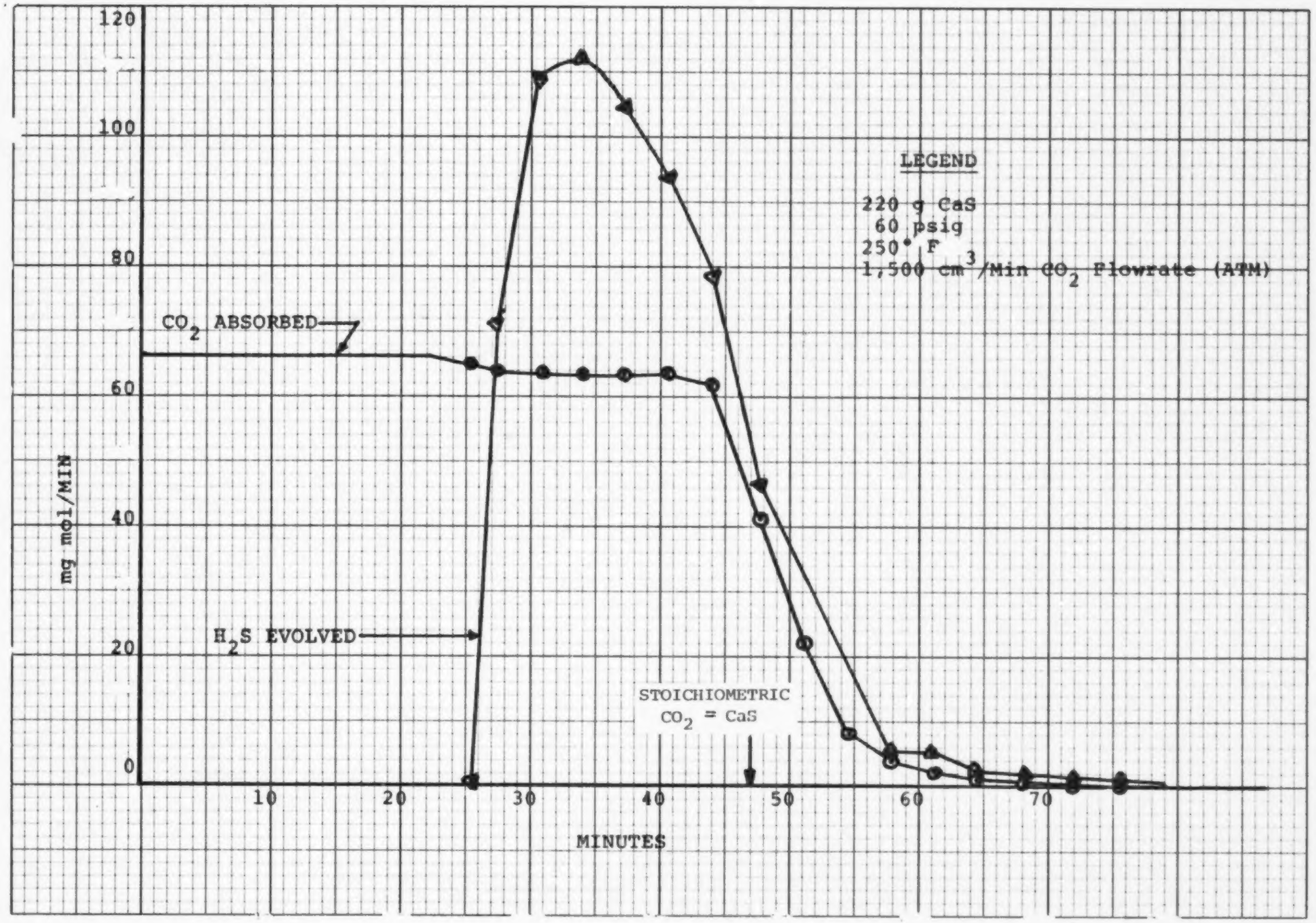

Figure 27.- Carbonation run 28, 3 liter slurry (7.3% solids).

An effort was made to "decode" the apparent experimental results by observing the following "rules of thumb":

1. It took 1.5 min for CO_2 to reach the reactor from the time (t = 0 min) the CO_2 valve was opened.
2. When H_2S was first detected at the sample port, the total amount of H_2S already generated, but accumulated in the system, would have been 0.4 g-mol (since H_2S is much heavier than He, a displacement type plug flow can be assumed for the H_2S flow.)
3. At any time when no CO_2 was detected in the sample port, the implication is that no CO_2 was evolved from the slurry "some time" ago. The "some time" is the time necessary for a total H_2S flow amounting to 0.4 g-mol.
4. The tail ends of both curves demonstrate perfect first order characteristics. It may be explained by the purging of inventory H_2S in the system with a constant CO_2 flow.

4.2.4.2 Reaction mechanism.- In all four runs, H_2S evolution was not detected until 20 to 30 min after CO_2 feed was started. It appears to suggest an initial stage of CO_2 absorption with no gas evolved followed by a reaction stage during which H_2S was generated. The following two-stage reaction mechanism has been conceived based on such experimental observation:

$$\begin{array}{lll} (1) & & CaO + H_2O + CO_2 \rightarrow CaCO_3 + H_2O \\ & \text{Stage 1} \left\{ \begin{array}{l} \\ \\ \end{array} \right. & \\ (2) & & 2CaS + H_2O + CO_2 \rightarrow CaCO_3 + Ca(HS)_2 \end{array}$$

$$(3)\ \text{Stage 2}\ \{\ Ca(HS)_2 + H_2O + CO_2 \rightarrow CaCO_3 + 2H_2S$$

Calculations indicate that Stage 1 absorption and stage 2 reaction are not completely separated with respect to reaction time; i.e., Stage 2 reaction starts whenever substantial amounts of $Ca(HS)_2$ have been produced in Stage 1. This is typical of a consecutive reaction system with $Ca(HS)_2$ as a reaction intermediate. Some calculations are shown below to demonstrate such an overlap:

1. Reduced sludge run 20--When H_2S was first detected at t = 21 min, CO_2 absorbed = 0.065[a] g-mol/min x (21 - 1.5[b]) = 1.27 g-mol. If Stage 1 absorption had completed, it would have absorbed 1[0.93[c]] + ½[1.18[d]] + ½[0.4[e]] = (1.72) g-mol of CO_2.

   Therefore, at this time (t = 21 min), Stage 1 absorption is

$$\frac{1.27 - \frac{1}{2}[0.4]}{1[0.93] + \frac{1}{2}[1.18]} = 70\% \text{ completed}$$

---

[a] corresponding to 1,500 cm^3/min CO_2 feed rate.

[b] 1.5 min for CO_2 to reach reactor.

[c] 0.93 g-mol of CaO in the 220 g sludge.

[d] 1.18 g-mol of CaS in the 220 g sludge.

[e] 0.4 g-mol of H_2S accumulated in the system.

2. Reduced sludge run 21--H_2S was first detected at t = 26 min, CO_2 absorbed = 0.065 x (26 - 1.5) = 1.59 g-mol.

   Stage 1 absorption is

$$\frac{1.59 - \frac{1}{2}[0.4]}{1\ [0.93] + \frac{1}{2}[1.18]} = 91\%\ \text{completed}$$

3. Pure CaS run 22 - H_2S was first detected at t = 25 min, CO_2 absorbed = 0.065 x (25 - 1.5) = 1.53 g-mol.

   Stage 1 absorption is

$$\frac{1.53 - \frac{1}{2}[0.4]}{\frac{1}{2}[3.05^{f}]} = 87\%\ \text{completed}$$

4. Pure CaS run 28--H_2S was first detected at t = 25 min, CO_2 absorbed = 1.53 g-mol and Stage 1 absorption is 87% completed.

4.2.4.3 Reaction rates.- The Stage 1 absorption rate is apparently limited by the rate at which CO_2 can be fed into the reactor in all the four runs. The implication is that the time required can be shortened by using some higher CO_2 feed rate until eventually a point is reached where other factors become controlling.

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[f] 3.05 g-mol of CaS in 220 g solids.

In present experiments, the CO_2 feed rate used is 0.065 g-mol/min for 3-liter slurry (containing 220 g solids) or 0.02 g-mol/min-liter.

To obtain the Stage 2 reaction rate, we have to find out the time when Stage 1 absorption has been completed. This time, t(min), can be calculated from the following equation:

$$0.065(t - 1.5) = 1[CaO^{a}] + [CaS^{b}] + [0.4 + \tfrac{1}{2}H_2S^{c}] \tag{4}$$

Equation (4) implies that total CO_2 absorbed at the time, t, should be accounted for by the total CO_2 capacity of Stage 1 and any CO_2, consumed in Stage 2. Using this relation, we found t ~ 31 min for the two CaS runs to complete stage 1 absorption, and t ~ 35 min for the two sludge runs.

For the two sludge runs (20, 21), after 35 min, CO_2 started to evolve from the slurry. The second stage reaction might be near completion; the rate, therefore, would not be obvious from Figures 24 and 25.

The two CaS runs (22, 28) reveal clearer information. After 31 min, stage 1 absorption was essentially completed; however, CO_2 was still absorbed at the rate it was fed for another 8 to 10 min. Corrections for time lag have been included in the above interpretation of experimental results. Thus, it appears that the Stage 2 reaction rate is also limited

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[a] CaO in the initial reactor charge, g-mole.
[b] CaS in the initial reactor charge, g-mole.
[c] Total H_2S evolved up to t min as can be integrated in Figures 24 through 27.

by the CO_2 feed rate, at least for the CaS runs. Also, the stoichiometry of H_2S to CO_2 (2 to 1), after 31 min, agrees exactly with reaction (3).

Batch experimental data from other sources indicate the Stage 2 reaction was of zero order with rates ranging from 0.01 to 0.1 g-mol of $Ca(HS)_2$/liter-min depending upon the mass transfer characteristics of the system. It implies a potential for increasing the reaction rate above the 0.02 g mol/liter-min (limited by CO_2 feed rate) from our current experiments. This possibility will be explored later during the pilot plant stage.

4.2.4.4 Material balance.- CO_2 material balance has been satisfied within the experimental error according to the following equation:

(5) Total $[CO_2]$ absorbed in g moles = [CaO] + [CaS],

where [CaO] and [CaS] are initial charges of CaO and CaS in g-moles, respectively.

The sulfur balance is poor for both the reduced sludge and the pure CaS runs. For reduced sludge runs, total $[H_2S]$ evolved in g-moles is approximately 82% [CaS]. For pure CaS runs, the total $[H_2S]$ evolved is approximately 71% [CaS].

However, analyses of the limestone product slurry after the experiments showed complete conversion of CaS (less than 1% CaS remaining in the solids). Therefore, the problem of sulfur imbalance has not been pursued further.

4.2.4.5 Effect of temperature and pressure.- Reactions rates in the present experiments showed little change within the ranges of temperature and pressure studied. This is probably due to the CO_2 feed rate limitation discussed previously.

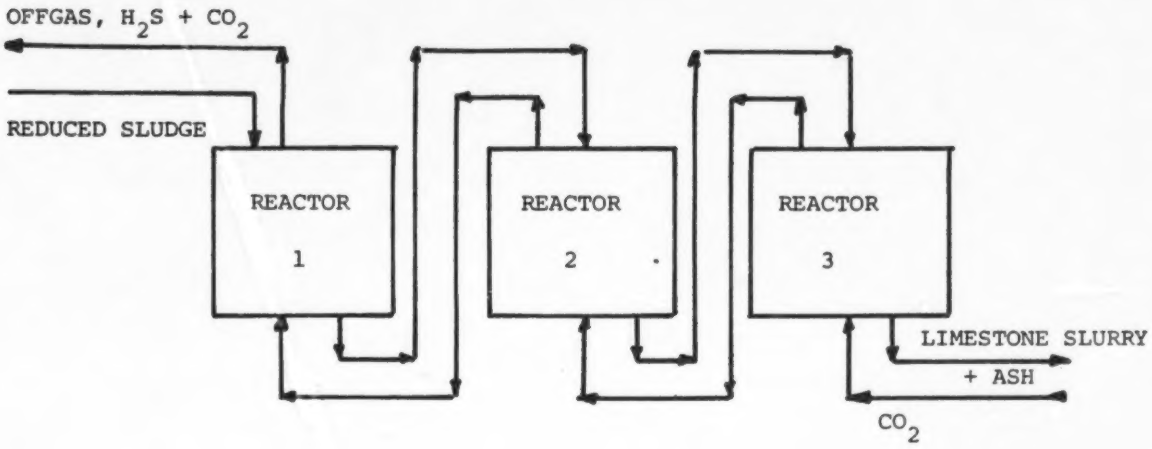
Data from other sources also indicated that both the absorption and the reaction rates are insensitive to temperature under atmospheric operations but mass transfer limitation was given as the explanation.

4.2.5 Pilot Plant Reactors

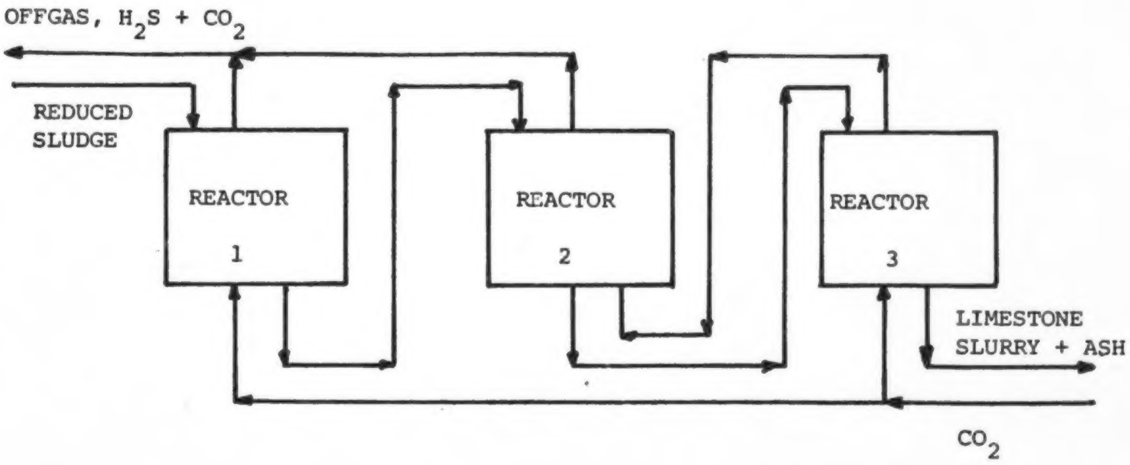
Based on above analyses, we believe that basic information has been obtained for the design of a pilot plant carbonation reactor system.

Three reactors in series with approximately 60 min of total residence time appears to be suitable for the pilot plant operation. The first two reactors are expected to achieve almost complete conversion of the reduced sludge. The third reactor would eliminate any unconverted CaS from the two preceding reactors.

The three reactor pilot plant system will also be able to provide different modes of operation based on the kinetic information obtained from the bench scale runs. For example, CO_2 can be fed from one end while sludge slurry enters from the other end, constituting a true countercurrent mode of operation.


OFFGAS, $H_2S + CO_2$
REDUCED SLUDGE
REACTOR 1
REACTOR 2
REACTOR 3
LIMESTONE SLURRY + ASH
CO_2

Alternatively, CO_2 can be fed into separate reactors, with each reactor performing a different function:


OFFGAS, $H_2S + CO_2$
REDUCED SLUDGE
REACTOR 1
REACTOR 2
REACTOR 3
LIMESTONE SLURRY + ASH
CO_2

In this mode of operation, Reactor 1 will carry out most of the Stage 1 absorption, leaving Stage 2 reaction completed in Reactor 2. Final cleanup of the product slurry will be achieved in Reactor 3.

Concentration of H_2S in the offgas should be high for the Claus plant operation. However, an optimum will have to be considered from the overall economics of the integrated system - the SO_2 scrubber, the Kel-S unit, and the Claus plant together.

4.3 FLOTATION TESTS

4.3.1 Apparatus and Procedure

The air flotation tests were performed at the Denver Equipment Ore Testing Facilities, Denver, Colorado. The air flotation feed sample was prepared at the Kellogg R&D Center by carbonating reduced sludge which was produced at the Kennedy Van Saun pilot kiln. The reduced sludge was obtained from the kiln discharge during the K1 kiln test.

The flotation tests were performed in a Denver Laboratory with a Model D-12 Flotation Machine (a batch flotation unit) using 250 and 500 ml batches.

Air flotation is a solid/solid separation technique, usually used in the mining industry in benefication of low-grade ores. It operates on the principle of air bubbles preferentially attracting and lifting selected solids to the surface of a liquid. The bubbles and solids then form a froth which is collected. Solid particles not selectively attracted by the air bubbles stay in the liquid. Flotation additives are usually introduced to enhance separation. Typical additives for non-sulfide, non-metallic, and metallic oxide ores include:

- Fatty acids
- Petroleum sulfonates
- Sodium salts of sulfonated long chain alcohols
- Amines

A single batch experiment consisted of:

- Placing the slurry in the tank.
- Agitating the slurry.
- Introducing additive.
- Starting the flotation air (which enters through the stirrer).
- Collecting the froth in a pan.

A multistage flotation process can be simulated by refloating either the froth or the liquid remaining in the tank. The air flotation experiments performed by Denver consisted of from two to four floats. Multistage flotation also permits the option of using a different additive in each float.

4.3.2 Program

The usual procedure for a flotation test at Denver was to weigh out a certain amount of feed solid, slurry it with water, and use the flotation cell to separate the feed into four fractions (three floats).

Additives were introduced through an eyedropper and reported as pounds of additive used per ton of solids. The residence time for each float was also measured.

Each fraction was filtered, dried, and weighed. Each fraction was then analyzed for percent acid insolubles, which consisted of measuring the weight loss after heating for 10 min in 10% hydrochloric acid. This test should give a rough indication of the amount of calcium compounds ($CaCO_3$, $CaSO_4$, $CaSO_3$, CaO, CaS) in a sample. This is an important parameter since the purpose of the air flotation units is to remove any inerts which do not participate in the SO_2 removal process. The $CaCO_3$ and CaO react directly with SO_2 in the scrubber; $CaSO_4$ and $CaSO_3$ are reduced to CaS in the kiln; and CaS is carbonated in the carbonation reactors. The calcium-rich stream is recycled back to the SO_2 scrubber, while the inerts are rejected to prevent them from building up in the system.

The acid insoluble test was done immediately after each air flotation test so that the results could be used to guide the next test.

Kellogg analytical services analyzed the sample weight percent of $CaCO_3$, CaS, $CaSO_4$, $CaSO_3$, CaO, Al_2O_3, FeO, SiO_2, free carbon, and MgO since this list included all compounds of interest. There are also undefined impurities which do not contain calcium or carbon and can be lumped with Al_2O_3, FeO, SiO_2, and MgO. These tests were done on "once through" material, in contrast to a commercial plant where the inerts would slowly build up to a higher level, a level that would be dependent on the inert rejection rate.

Denver Equipment can perform tests to study the effect of inerts recycle which will increase the amount of inerts fed back to the air flotation unit. Denver

Equipment will be requested to perform these tests before pilot plant operation begins.

4.3.3 Results

Denver Equipment performed the 17 air flotation experiments listed in Table XI. Three different air flotation samples were prepared and sent to Denver Equipment Company. The first sample was produced by carbonating kiln product from kiln run K1. This product contained about 5 wt % free carbon and required a separate float to remove the carbon. Two later samples were prepared by carbonating product made from kiln run K2; these samples contained less than 0.1 wt % carbon and did not require a separate carbon float. The two low-carbon samples were carbonated by two different methods:

- A 14 wt % sample was contacted by CO_2.
- A 7 wt % sample was first contacted by H_2S, then contacted with CO_2 (to simulate a continuous process).

The two samples appeared to separate at about the same efficiency, and the 14 wt % used about one-half the additive dosages of the 7 wt % samples.

The first experiment used a fatty acid as promoter, which did not produce a good separation with a large amount of additive. The next 16 experiments used a promoter called AERO 845 marketed by American Cyanamid Company. This promoter gave separation of acid soluble and acid insoluble fractions. Pine oil was added as a frother to most of the tests. The manufacturer recommends the use of fuel oil with Aeropromoter 845 to decrease the amount of additive dosage for a required separation.

TABLE XI.- AIR FLOTATION RESULTS - DENVER EQUIPMENT COMPANY

					ADDITIVES #/TON SOLIDS							
Test No.	Feed	No. of Floats	Wt % Ca Recovery	Wt % Ash Rejection	Fatty Acid FA-2	Pine Oil	Sodium Silicate	Fuel Oil	Aeropro-motor 845	Dowfax 9N9	Aeropro-motor 839	Accoal Froth S-4005
1	High carbon 7 wt% solids	2	73	31	16.5	1.1						
2		2	59	64		0.5	4.0	4.0	9.7			
3		3	83	33		1.5	4.0	8.7	8.7			
4		3	60	68		0.5	6.0	4.5	9.0			
5		3	80	51		2.0		7.7	3.7			
6		3	93	30		2.6		3.8	2.0			
7		3	96	23		1.8		3.7	2.2	0.9		
8		3	87	47		3.0		5.2	2.6			
9		3	74	62					2.0		2.0	3.2
10		3	49	77				1.6	1.0		1.0	3.2
11		4	61	66		3.0		2.5	0.8	0.4	0.8	
12	Low carbon 7 wt% solids	2	43	86					6.1		1.4	
13		2	42	91				1.1	9.1			
14		3	94	30		1.6		2.1	2.1			
15	low carbon 14 wt% solids	3	86	40		0.70		1.0	1.0			
16		4	85	38		0.9		1.6	0.8			
17		2	76	52		0.9		1.5	1.5			

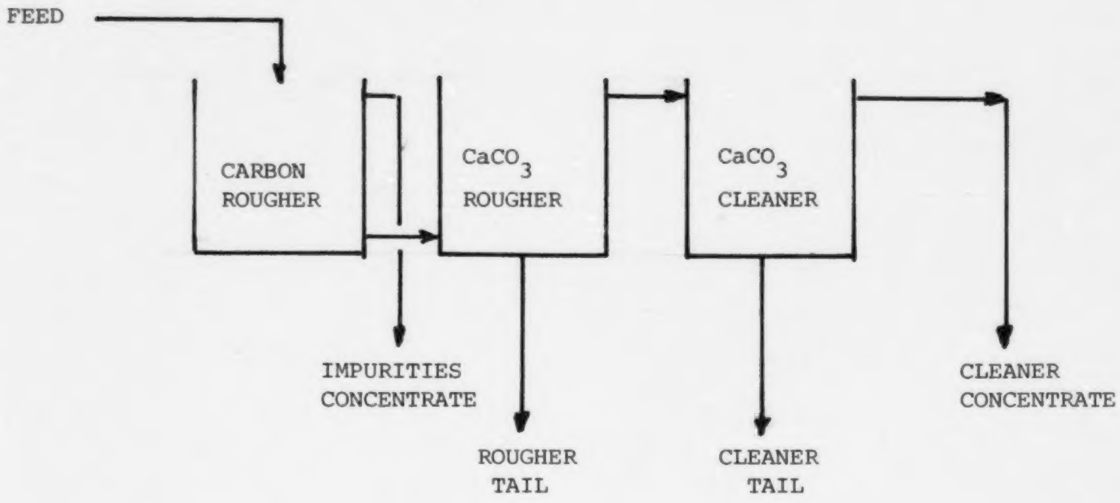
$$\%\ \text{Calcium Recovery} = \frac{\#\text{Ca in Ca-Rich Stream}}{\#\text{Ca Feed}}$$

$$\%\ \text{Ash Rejection} = \frac{\#\text{Ash in Ash-Rich Stream}}{\#\text{Ash Feed}}$$

Most of the additives would tend to adhere to the solids being floated and hence be recycled to the scrubber. Their vapor pressure and total amounts should be low enough to prevent sizable quantities being vaporized in the scrubber. All additives would be destroyed once they were recycled back to the Kel-S process in the rotary kiln. A fraction of the additives would be rejected from the Kel-S process with the ash and rejected calcium compounds. This could prove to be a problem in the eventual disposal of the ash/calcium carbonate mixture.

The flow scheme of a typical air flotation test is presented in Figure 28. The feed is separated into an impurities concentrate, rougher tail, cleaner tail, and cleaner concentrate in three successive floats. In the first float, the froth would be discarded commercially, while in the last two floats, the tails would be discarded. The calcium recovery is the percent of feed calcium remaining in the cleaner concentrate, while the impurities rejection is the percent of the feed impurities contained in the combination of the impurities concentrate, rougher tail, and cleaner tail.

Figure 28 also shows a comparison of the Denver and Kellogg solids analysis for Test 8. The Denver analysis resulted in a 86.6% calcium recovery and a 46.7% inerts rejection, while the Kellogg analysis determined a 88.7% calcium recovery and a 41.7% carbon plus inerts rejection, which is good agreement. The Kellogg analysis also showed that air flotation could be used to separate excess free carbon from the inerts and calcium compounds. The impurities concentrate


FEED
CARBON ROUGHER
$CaCO_3$ ROUGHER
$CaCO_3$ CLEANER
IMPURITIES CONCENTRATE
ROUGHER TAIL
CLEANER TAIL
CLEANER CONCENTRATE

Denver Analysis

	Wt % of Feed Solids	Acid Insolubles (wt%)
Impurities Concentrate	8.9	37.3
Cleaner Concentrate	81.6	9.8
Cleaner Tail	3.0	30.5
Rougher Tail	6.5	42.5
Total (Feed)	100.0	15.0

Kellogg Analysis

	Wt % of Feed Solids	Calcium Compounds (wt%)	Free Carbon (wt%)	Inerts (wt%)
Impurities Concentrate	8.9	60.2	29.8	10.8
Rougher Tail	6.5	42.1	3.7	54.2
Cleaner Tail	3.0	38.5	7.9	53.6
Cleaner Concentrate	81.6	87.9	2.4	13.6
Total (Feed)	100.0	80.9	5.1	17.1

Calcium Compounds: $CaCO_3$, $CaSO_4$, $CaSO_3$, CaO, and CaS

Inerts: Al_2O_3, FeO, MgO, SiO_2, and unidentified noncalcium and noncarbon containing compounds.

Figure 28.- Bench Scale Air Flotation Test 8
Denver Equipment Company

could then be recycled back to the kiln as a partial substitute for fresh coal.

Figure 29 shows the results of the ten experiments which used three floats. Experiment 2 used two floats and is not included. The figure shows that, as expected, calcium recovery and inert rejection are tied together strongly for a single additive and number of floats; i.e., increasing the calcium recovery will decrease the inert rejection.

The high carbon sample used for air flotation was carbonated and shipped to Denver before a complete analysis of the sample was available. The carbon content of the kiln discharge was determined to be 7.66%, the highest kiln discharge carbon content measured. The carbonation of the CaS and CaO would tend to decrease the total carbon wt % by increasing the amount of solids, so the 5.1% carbon in the air flotation feed seems reasonable. This high a carbon content was not expected and at first confused Denver. After a few experiments, they found that an impurities float removed the bulk of the carbon.

4.3.4 Pilot Plant Units

Denver Equipment analyzed the results of the bench scale experiments and recommended three air flotation cells (cells of a unit have a common froth header, while the tails of each cell are sent to the adjacent cell) for the carbon rougher, four cells for the

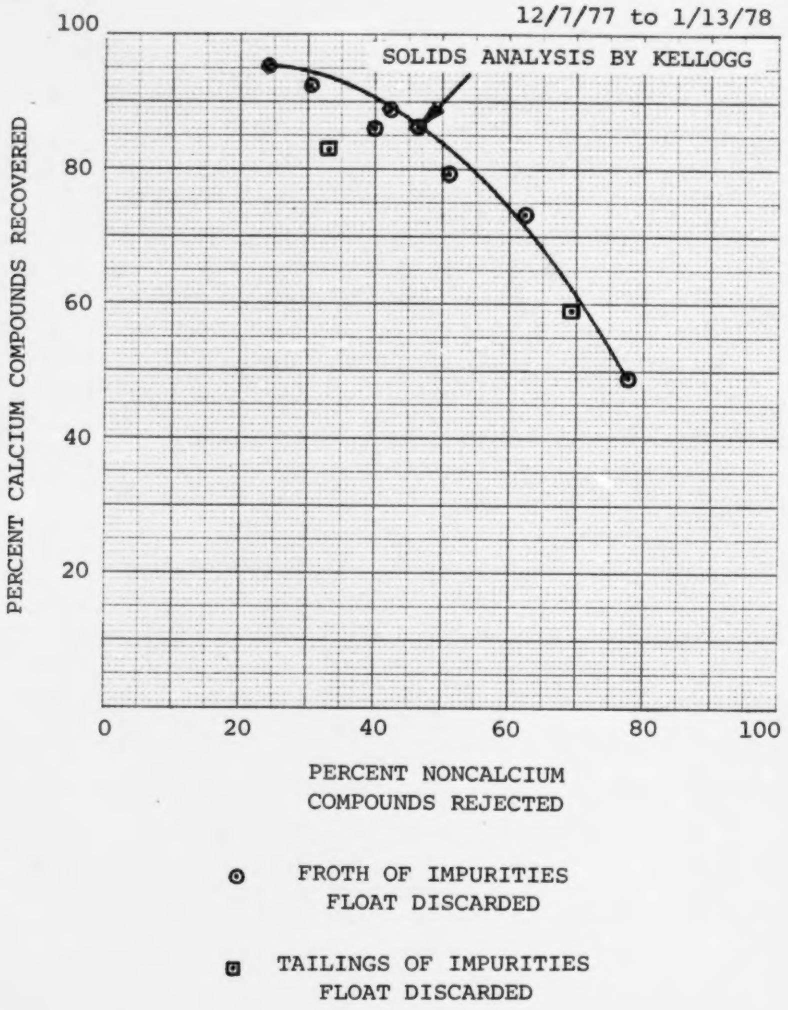


Figure 29.- Air flotation tests calcium recovery vs inerts rejection, Denver Equipment Company.

calcium carbonate rougher, and two cells for the calcium carbonate cleaner (see Figure 28). All cells should be the Denver cell No. 5 which has an effective volume of 0.4 ft^3/cell, and is the smallest continuous air flotation machine made by them. The cell is designed for pilot plant operation.

4.4 TWO-STEP TESTS

4.4.1 Introduction

The original Kel-S flowsheet (ca 1968) used a filter to remove ash from the scrubber/Kel-S loop and the original proposal to EPA (9 May 1975) was based on this unit operation for ash removal. The ash was filtered out of a $Ca(HS)_2/H_2O$ solution produced by reacting CaS with H_2S as follows:

(1) $$CaS(s) + H_2S \rightarrow Ca^{++} + 2HS^-$$

The recycle scrubber slurry was then produced by reacting the $Ca(HS)_2/H_2O$ solution with CO_2 and liberating H_2S for reaction (1). The reaction is:

(2) $$Ca^{++} + 2HS^- + CO_2 + H_2O \rightarrow CaCO_3(s)$$

Excess H_2S is sent to a standard design Claus sulfur recovery unit in a commercial plant.

Further process development indicated that Kel-S capital costs would be reduced and the flowhseet simplified if reactions (1) and (2) could be carried out in the same vessel according to the overall reaction:

(3) $$CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S$$

In this case, a unit operation would have to be found to separate ash from $CaCO_3$. Reaction (3) was demonstrated in bench scale equipment. Air flotation was selected as the unit operation because the purification of calcite by air flotation is a commercial mining operation. The revised proposal (3 December 1976) was based on the new "one step" process. This proposal was accepted and became contract 68-02-2644.

Air flotation proved to be only a marginally acceptable unit operation for ash removal since sizable amounts of calcium values were lost with the rejected ash. Air flotation also required the addition of air flotation additives which might make the rejected ash unsuitable for landfill.

Kellogg then decided to reexamine the use of the two-step process in the Kel-S process to avoid the use of additives.

4.4.2 Dissolution and Carbonation Tests

The dissolving and carbonation reactions were studied at the Kellogg R&D Center using the equipment and methods described in Section 4.2.1. A summary of the runs is presented in Table XII. The equipment was

TABLE XII.- TWO-STEP CARBONATION REACTIONS

		Second Step			First Step
Run No.	Starting Slurry Composition	CO_2 Feed Flow Rate l/min	%H_2S Max	Max H_2S Flow Rate l/min	H_2S Feed Flow Rate l/min
29	7.3% Sludge	1.5	98	2.8	0.8
33	7.3% CaO	6.0	91	9.8	1.7
34	7.3% Sludge	6.0	91	9.0	1.7
37	7.3% Sludge	9.9	86	12.6	8.4

Conditions: First Step: 150° F, 15 psig

Second Step: 150° F, 35 psig

modified only to permit the introduction of H_2S into the reactor vessel.

Figure 30 shows the percent H_2S in the offgas as well as the flow of unreacted H_2S out of the vessel for Run 29. The point at which a stoichiometric amount of H_2S had been added is shown which satisfies the H_2S requirement of CaS according to (1) and the $Ca(OH)_2$ requirement according to:

(4) $$Ca(OH)_2 + 2H_2S \rightarrow Ca^{++} + 2HS^- + 2H_2O$$

The remaining solids were filtered. These solids contained no CaS and 16% of the feed calcium. The clear liquid had a Ca/S ratio of 1.93, close to the expected ratio of 2.0.

Reactions (1) and (4) occurred as fast as H_2S was fed to the reactor, up to the maximum flow rate of 8.4 l/min. These reactions would be expected to be at least as fast as the smiilar reactions with CO_2.

The liquor was then contacted in the autoclave with CO_2 using the same procedure as carbonating the reduced sludge. Figure 31 shows the results of the carbonation of the filtered liquor produced in Run 29. The results are nearly identical to the carbonation of the reduced sludge in that the maximum H_2S production rate is about twice the CO_2 feed rate, a high percent H_2S was measured in the offgas, and the maximum H_2S rate came at about the time that a stoichiometric amount of CO_2 had been fed to the reactor.

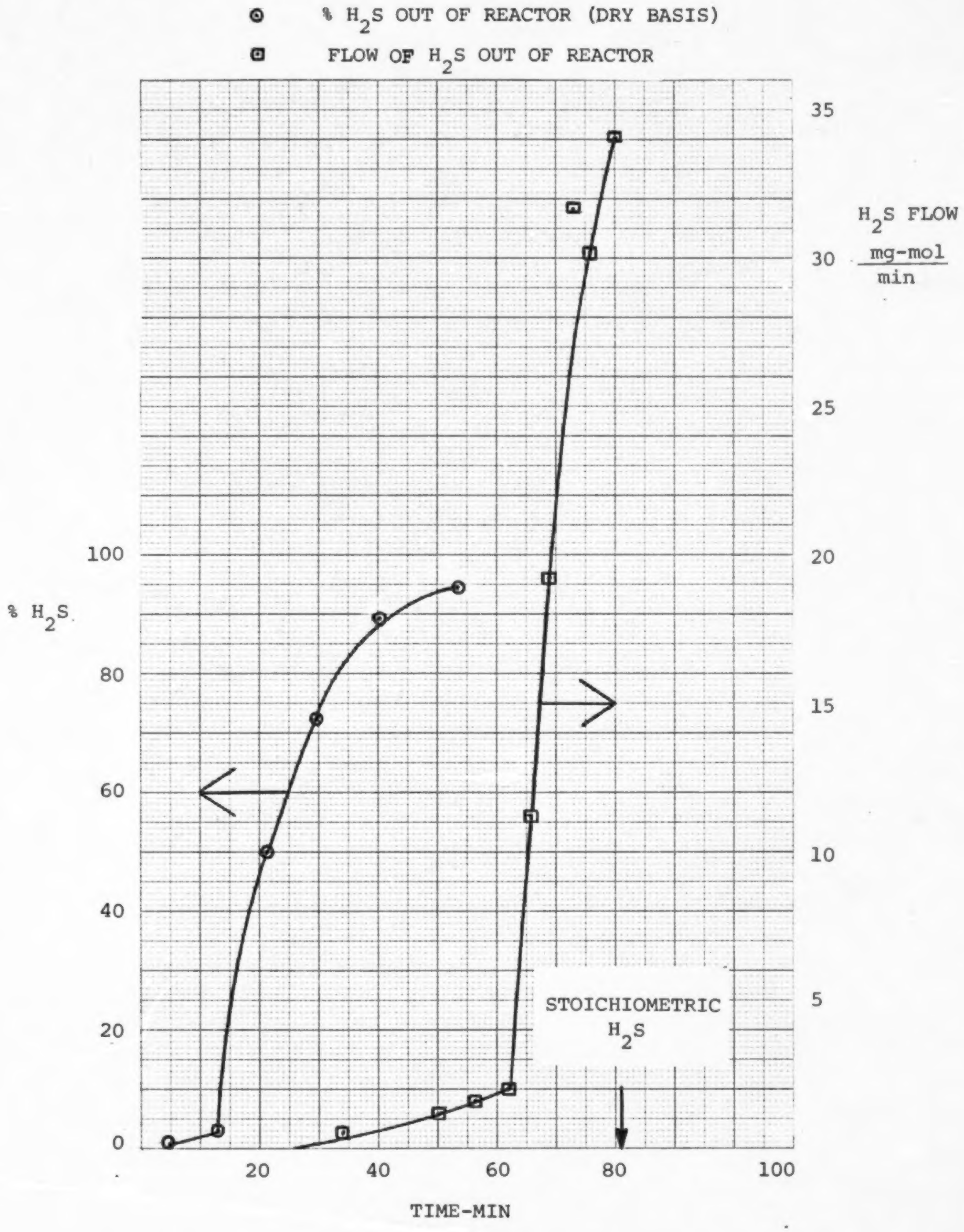


Figure 30.- Run 29, Dissolution, 3 liter slurry (7.3 wt % solids).

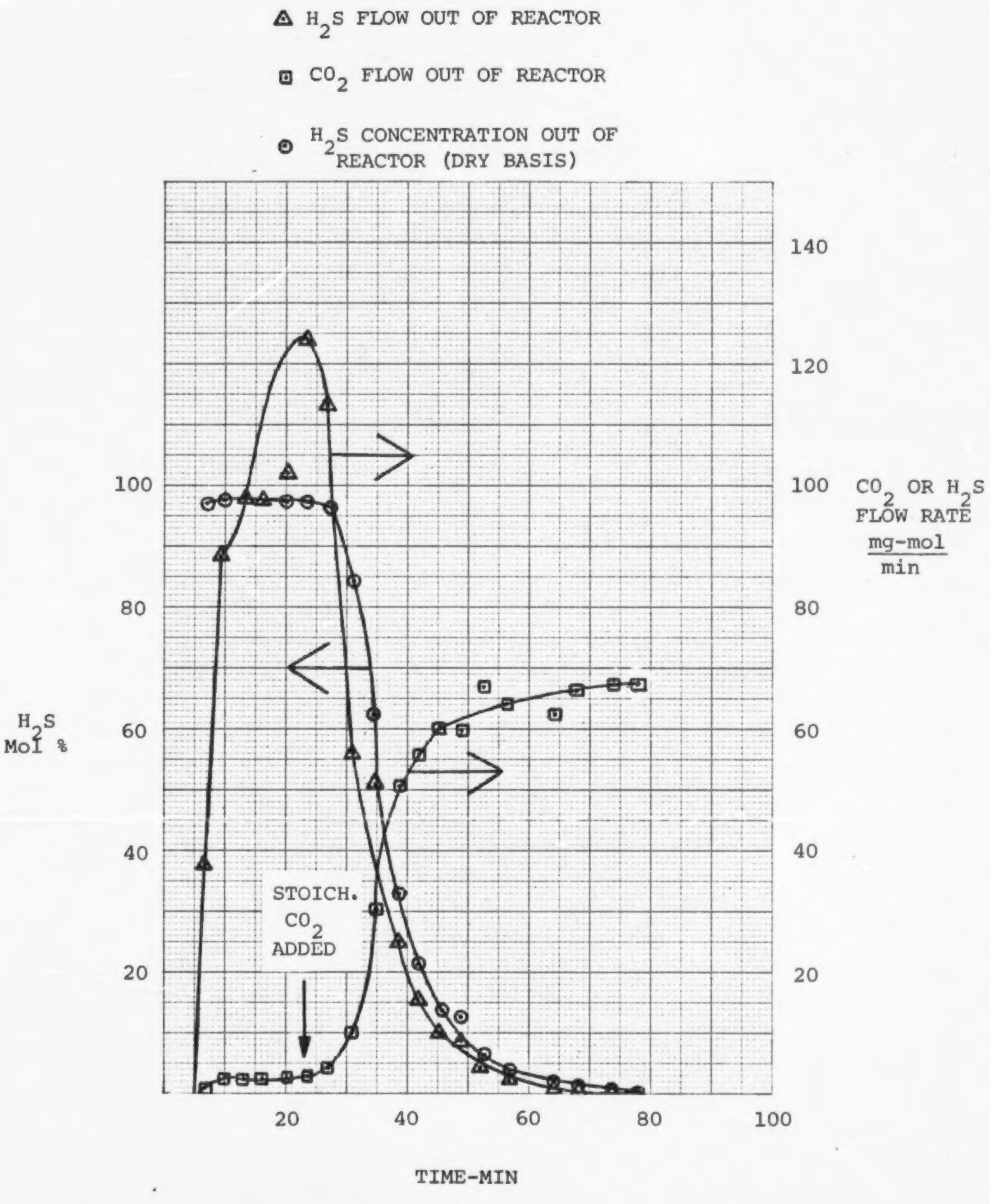


Figure 31.- Run 29 - Carbonation of $Ca(HS)_2$ solution.

The filtered ash and precipitated $CaCO_3$ were analyzed. The filtered ash contained 15.99% Ca^{++}, while the precipitated $CaCO_3$ was 99.37% calcium carbonate. Based on the weights of the ash and precipitated $CaCO_3$, the calcium yield to $CaCO_3$ was 77.4%. The filtered ash contained 16% of the starting Ca^{++}. The remaining Ca^{++} was lost with the water contained on the filter cake (10.83%). This Ca^{++} could be recovered by washing the cake more thoroughly.

4.4.3 Filtration and Centrifugation Tests

Bird Machine Company, South Walpole, Mass. agreed to run filtering and centrifuging tests on samples of H_2S-treated, reduced sludge. A 3-gallon sample was prepared at the Kellogg R&D Center and sent to Bird Machine Company.

Bird Machine Company ran five types of tests on the sludge samples:

o Test tube centrifuge test to determine the effect of temperature, residence, time, and flocculant dosage on the separation efficiency and the cake condition - The separation efficiency was reported as (cc of cake/cc of original sample) and the cake condition reported as the height of cake that could support a glass rod. Each spin test was concluded when the liquor above the cake was clear and nearly the entire cake could support the rod. These tests gave guidance to the best conditions for later centrifuge tests.

- Solid bowl batch centrifuge tests on a 5.2" diameter bowl - The test was run by pouring about 700 ml of sample into a solid bowl rotating on a vertical axis; the cake collected on the inside of the bowl, while the liquid overflowed the bowl, and was collected. The surface water on the cake was then removed by a vacuum hose. The cake produced was manually scraped off the inside of the bowl at the conclusion of the test. The cake quality produced by this test is approximately the same as would be produced in a continuous bowl centrifuge. The results are reported in Table XIII.

- Perforated bowl batch tests were performed in the same machine as the solid bowl tests, except that the solid bowl was replaced by a perforated bowl covered by a cloth. Past experience has shown that the percent solids recovered on a continuous solid bowl centrifuge would lie between the solid bowl results and the perforated bowl results. The results of the perforated bowl tests are shown in Table XIII.

- Vacuum filter batch tests were performed to determine the filtering rate. The tests were conducted in a 80 cm^2 filter on a batch basis using different amounts of feed slurry; the time to cake dryness was measured. The results of the vacuum filter tests are given in Table XIII.

- Vacuum filter batch tests with washing - The "optimum" batch amount of slurry was filtered, and washed with water. The results are given in Table XIII. The time given is the wash time plus the

TABLE XIII.- CENTRIFUGE AND FILTER RESULTS - BIRD MACHINE COMPANY
(22 MARCH 1978)

CENTRIFUGE	Temperature °C	Flocculant Dose #/Ton Solids	Feed Solids wt%	Cake wt% Solids	Liquor wt% Solids	Ash Rejection %
Solid Bowl	20	0.0	3.11	30.14	0.185	94.6
Solid Bowl	65	0.0	3.11	37.45	0.161	95.2
Solid Bowl	65	0.2	3.11	34.17	0.051	98.5
Solid Bowl	65	0.6	3.11	42.51	-	-
Perforated Bowl	20	0.0	3.11	44.98	0.416	87.7
Perforated Bowl	65	0.2	3.11	44.30	0.179	94.6

Flocculant used was Percol 725

FILTER	Feed ml	Cake Solids wt%	Time Sec.	Filter Rate #solids/hr-ft^2
Vacuum Filter	100	44.60	13	22.0
Vacuum Filter	200	44.68	17	33.7
Vacuum Filter	300	46.10	28	30.7
Vacuum Filter (washed with 250 ml H_2O)	250	36.91	70	10.2

All filter tests done at 65° C

filtering time. The flocculant used was Percol 725, an anionic polymer flocculant marketed by Allied Colloids.

The tests indicate that better calcium recovery and ash rejection can be expected from both centrifuges and filters than obtained with air flotation units. Centrifuge and filter tests resulted in good separations without the use of additives, which add to their advantage over air flotation, since additives might prevent the disposal of ash as landfill.

The preliminary centrifuge results indicate no dramatic improvement with flocculant and, therefore, the use of flocculant is not justified. The centrifuge gave satisfactory separation at 149° F which indicates that cooling will not be required between the dissolving reactor and the centrifuge, and heating will not be required between the centrifuge and the carbonation reactor.

4.4.4 Process Comparison

A flowsheet of the one-step and two-step processes is shown in Figure 32. The two-step process requires an extra reactor to clean up the recovered cake (mostly ash) because the water contained in the cake contains dissolved $Ca(HS)_2$. The two-step process sends nearly pure $CaCO_3$ back to the scrubber, while the one-step process sends $CaCO_3$ and some ash back to the scrubber, thus increasing the total amount of solids recirculated through the scrubber/Kel-S loop.

The economics of the two processes are compared on the following basis:

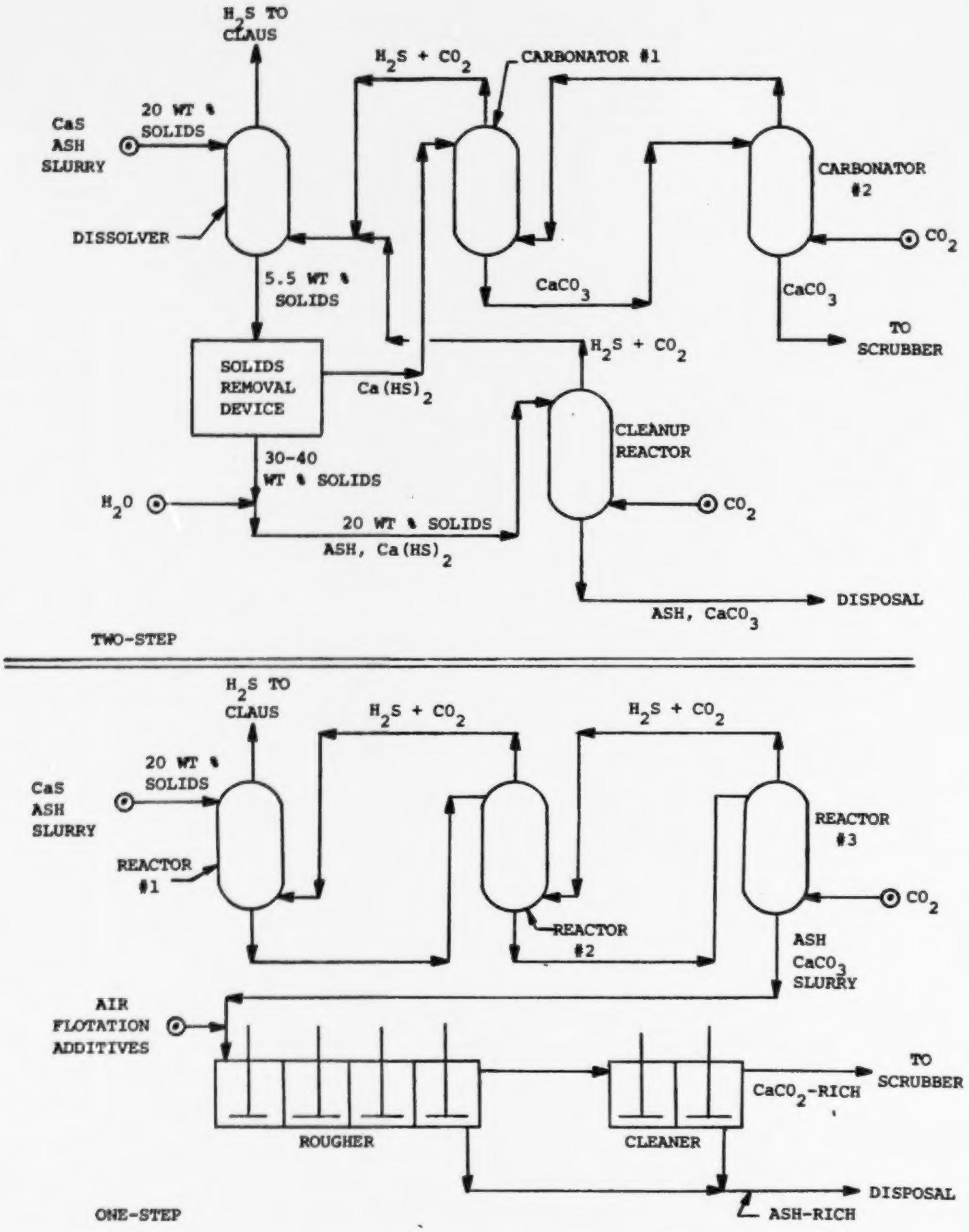

H_2S TO CLAUS
$H_2S + CO_2$
CARBONATOR #1
CaS ASH SLURRY
20 WT % SOLIDS
DISSOLVER
5.5 WT % SOLIDS
CARBONATOR #2
CO_2
$CaCO_3$
$CaCO_3$
TO SCRUBBER
SOLIDS REMOVAL DEVICE
$Ca(HS)_2$
$H_2S + CO_2$
CLEANUP REACTOR
30-40 WT % SOLIDS
H_2O
CO_2
20 WT % SOLIDS
ASH, $Ca(HS)_2$
DISPOSAL
ASH, $CaCO_3$
TWO-STEP
H_2S TO CLAUS
$H_2S + CO_2$
$H_2S + CO_2$
CaS ASH SLURRY
20 WT % SOLIDS
REACTOR #1
REACTOR #2
REACTOR #3
CO_2
ASH $CaCO_3$ SLURRY
AIR FLOTATION ADDITIVES
ROUGHER
CLEANER
$CaCO_2$-RICH
TO SCRUBBER
DISPOSAL
ASH-RICH
ONE-STEP

Figure 32.- Process comparison, one step and two step processes.

- 500 MW - sized scrubber/Kel-S unit
- Equal amount of ash rejected from the system (forcing the recycle stream to increase)
- $CaCO_3$ rejected with the ash is made up at \$10/ton.
- 10% excess CO_2 must be sent to the final carbonation reactor in insure no CaS or $Ca(HS)_2$ is recycled to the scrubber.
- Bench scale tests can be scaled up to commercial size equipment.

The 10% excess CO_2 requirement is a detriment to the two-step process because most of the CO_2 reaching the dissolving tower will react with CaS or $Ca(HS)_2$ to form $CaCO_3$, which will then be rejected from the process with the ash by the solids removal device. In the one-step process, however, the 10% excess CO_2 flows through the three reactors to the Claus plant.

The results of the economic analysis are shown in Table XIV. One centrifuge would be required for a 500 MW plant. One extra centrifuge would be required for cake washing, since Bird Machine Company does not believe that the cake is suitable for washing in the centrifuge. Three vacuum filters would be required for a 500 MW plant.

The air flotation units have the lowest ash separation capital cost, but the poorest ash/$CaCO_3$ separation efficiency, leading to a higher operating cost for makeup $CaCO_3$, and a higher capital cost for the other Kel-S equipment due to the higher amount of ash recycle. The added detriment of air flotation

TABLE XIV.- ECONOMIC ANALYSIS

METHOD	Approximate Capital Cost $M	% Feed $CaCO_3$ Recovered	% Feed Ash Rejected	Makeup $CaCO_3$ $M/Y	Additives $M/Y	Σ $M/Y	Notes
ONE STEP							
Air Flotation Expt. 17	65	76	52	414	307	721	Additives: Pine Oil, Fuel Oil, Aeropromotor 845
Air Flotation Expt. 9	110	74	62	455	643	1098	Additives: Aeropromoter 839 and 845, Accoalfroth S-4005
TWO STEP							
Centrifuge	200	77	92	402	none	402	
Centrifuge (washed)	400	86	84	243	none	243	Cake reslurried and recentrifuged
Centrifuge	200	74	97	455	33	488	Additive: Percol 725 0.2 #/T
Centrifuge (washed)	400	83	93	288	33	321	Additive: Percol 725 0.2 #/T, cake reslurried and recentrifuged
Filter	900	79	100	363	none	363	
Filter (washed)	900	90	100	172	none	172	Cake washed on filter

Note: $M = $1,000

additives which are expensive (Aeropromoters 845 and 839, Accoalfroth S-4005) or contaminate the disposed ash (fuel oil, pine oil) makes either centrifuging or filtering the superior ash removal method.

Centrifuges have an edge over filters because of their lower capital costs.

The use of flocculant does not appear economically attractive due to the poorer calcium recovery. Flocculant might also contaminate the ash product. It does appear, however, that an extra centrifuge for washing can be justified.

Based on all available data to date, it is concluded that centrifugation is the best unit operation step for the removal of calcium carbonate from fly ash, pelletizing additives, and other inerts. This decision requires the use of the two-step process in the EPA/Kel-S pilot plant.

4.4.5 Pilot Plant Units

Bird Machine Company has a small 6 inch centrifuge available for rental, which will be used in the pilot plant to confirm the bench scale batch experiments on a continuous basis. The unit is rated at liquid feed rates from 0.1-10 GPM.

The pilot plant will not contain a cleanup reactor; the recovered solids will be reslurried with water and stored. The stored solids will then be contacted with CO_2 countercurrently in the pilot plant carbonators to remove any dissolved sulfur as H_2S. The ash solids will then be sulfur free and can be disposed.

GLOSSARY

SELECTIVITY: The percent sulfur in the product which is in the form of CaS.

YIELD: The percent sulfur in the starting material which is observed as CaS in the product.

SULFUR BALANCE: The ratio of sulfur in the product to that in the starting material.

COAL CONVERSION: Percent of total carbon in the coal which was used during the reaction.

$$\frac{\text{Total carbon-carbon in product}}{\text{total carbon}}$$

COAL EFFICIENCY: The ratio of the amount of carbon required to obtain the product to the amount of total carbon in the coal.

APPENDIX A

ALLIS-CHALMERS
BALLING TESTS
ON
A SAMPLE OF SCRUBBER SLUDGE

ALLIS-CHALMERS
PROCESS RESEARCH AND TEST CENTER
9180 FIFTH AVENUE
OAK CREEK, WISCONSIN

BALLING TESTS

For

PULLMAN KELLOGG

DIVISION OF PULLMAN INCORPORATED

On

A SAMPLE OF SCRUBBER SLUDGE

Test Center Project No. 77-185

Charge No. 01-8489-71439

FORM 7669-3
LITHO IN U.S.A.

Dates Performed: Oct. 14, 18, 25, 1977

Date Reported: December 9, 1977

Reported by: R. R. Kucik

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INTRODUCTION

Balling tests were conducted for Pullman Kellogg on a sample of scrubber sludge at the Allis-Chalmers Process Research & Test Center, Oak Creek, Wisconsin. The tests were conducted on October 14, 18, and 25, 1977. The tests were requested jointly by Dr. B. J. Mandelik, Process Manager - Inorganic Chemicals Division and Mr. Wayne Talbert, Project Manager KeL-S Process, of the Pullman Kellogg Research and Development Center, Houston, Texas. The project was assigned Test Center Project No. 77-185 and charges were accumulated against Order No. 01-8489-71439.

The test objectives were to determine the expected green ball qualities from a mixture of [redacted][1] scrubber sludge and [redacted][1] coal.

(1) without additives

(2) with 0.75% bentonite added

(3) with 3.0% bentonite added

Also, a secondary objective was to determine, if possible, the differences in the test sludge and the previous sludge tested in the Allis-Chalmers Test Center Project No. 74-154.

MATERIAL DESCRIPTION

A total of three 5 gallon cans containing approximately 135 pounds of the scrubber sludge was received at the Test Center on October 14 and October 20, 1977. The moisture content of the material was 16.05% (when dried @ 105 °C).

The coal used for preparing the [redacted][1] blend for pelletizing was an anthracite coal containing 0.21% moisture and ground to 82.47% -200 mesh.

Size analyses of the sludge may be found at the conclusion of this report. It is noted that the wet-dry screen analysis conducted was thought to be in error due to the water solubility of the sludge. The sedigraph analysis was more accurate because water was not used as the dispersant.

FORM 7669-3
LITHO IN U.S.A.

---

[1] Confidential data

TEST PROCEDURES AND EQUIPMENT USED

Mixing:

Apparatus

The blending of the coal, scurbber sludge and bentonite (where applicable) was accomplished in a miniature mix muller 31 cm in diameter by 18 cm deep.

Procedure:

	Test 1	Test 2	Test 3
[redacted][1]	[redacted][1]	[redacted][1]	[redacted][1]
% Bentonite	-	0.75	3.0
% Moisture	As Req'd. →		

Calculations were made on dry basis. The quantity of water required to raise the moisture of the blends to 23-24% was added in the course of 1 minute. The bentonite (when applicable) was added in a 2 minute time period, whereupon the mixer was run for an additional 0.5 minutes.

Seed Balling:

Apparatus

The seed balls were produced in a 36 cm diameter by 25 cm deep open ended balling pan oprating at 52 rpm and 54 degrees from the horizontal.

Procedure

Balling time	5 minutes
Feed rate	0.25 kg/min.

The quantity of water is sprayed on. Quantity of seeds 3.5-5 mm required for balling is 240 grams.

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LITHO IN U.S.A.

---

[1] Confidential data

Balling:

Apparatus

The green balls were prepared in a 1 meter diameter by 165 mm deep balling pan operating at 20 rpm and 47 degrees from the horizontal.

Procedure

Balling time	4 minutes
Feed rate	1750 gms/min.

The quantity of water is sprayed on. The diameter of green balls used for physical testing shall be 11.1 x 12.7 gm.

Green Ball Testing:

Compression Tests

Twenty (20) green balls of the 11.1 x 12.7 mm size were broken using a motorized Chattilon Compression tester operating at a platten speed of 20 mm/in. The range of the scale was 0-4.54 kg.

Drop Tests

Twenty (20) green balls of the 11.1 x 12.7 mm size were repeatedly dropped from a height of 45 cm, until cracks appeared on the balls. The number of drops were recorded on a log.

FORM 7669-3
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BALLING TEST SUMMARY

	Test 1 No Additive	Test 2 0.75% Bentonite Additive	Test 3 3.0% Bentonite Additive
Pan Feed Moisture %	23.75	23.00	23.25
Green Ball Moisture %	24.00	24.23	24.55
Avg. Green Ball 45 cm (18") Drop Number	5.45	4.85	14.55
Avg. Green Ball Compr. Str. - kg (lbs)	0.68 (1.49)	0.65 (1.43)	0.82 (1.80)
Avg. Dry Ball Compr. Str. - kg (lbs)	0.44 (0.98)	0.82 (1.80)	5.70 (12.56)

CONCLUSIONS

The data from the above tests suggests that the material is different in chemistry and size consist than the material used for T/C Project 74-154. However, suitable green balls may be prepared from this material by grinding the material finer or with the addition of bentonite.

Roy Kucik
R. R. Kucik
Process Research & Test Center
MINERALS PROCESSING GROUP

APPENDIX

FORM 7669-3
LITHO IN U.S.A.

PULLMAN KELLOGG

Scrubber Sludge As Received Sedigraph Results
(10-26-77)

Mesh Size	Micron Size	% Passing
65	210	97.0
100	149	94.5
150	106	92.0
200	75	89.5
270	53	83.0
325	45	77.5
400	38	72.0
500	26	58.0
	20	47.5
	15	39.0
	10	28.5
	8	23.5
	6	18.0
	4	11.5
	2	6.0
	1.5	4.0

FORM 766P-3
LITHO IN U.S.A.

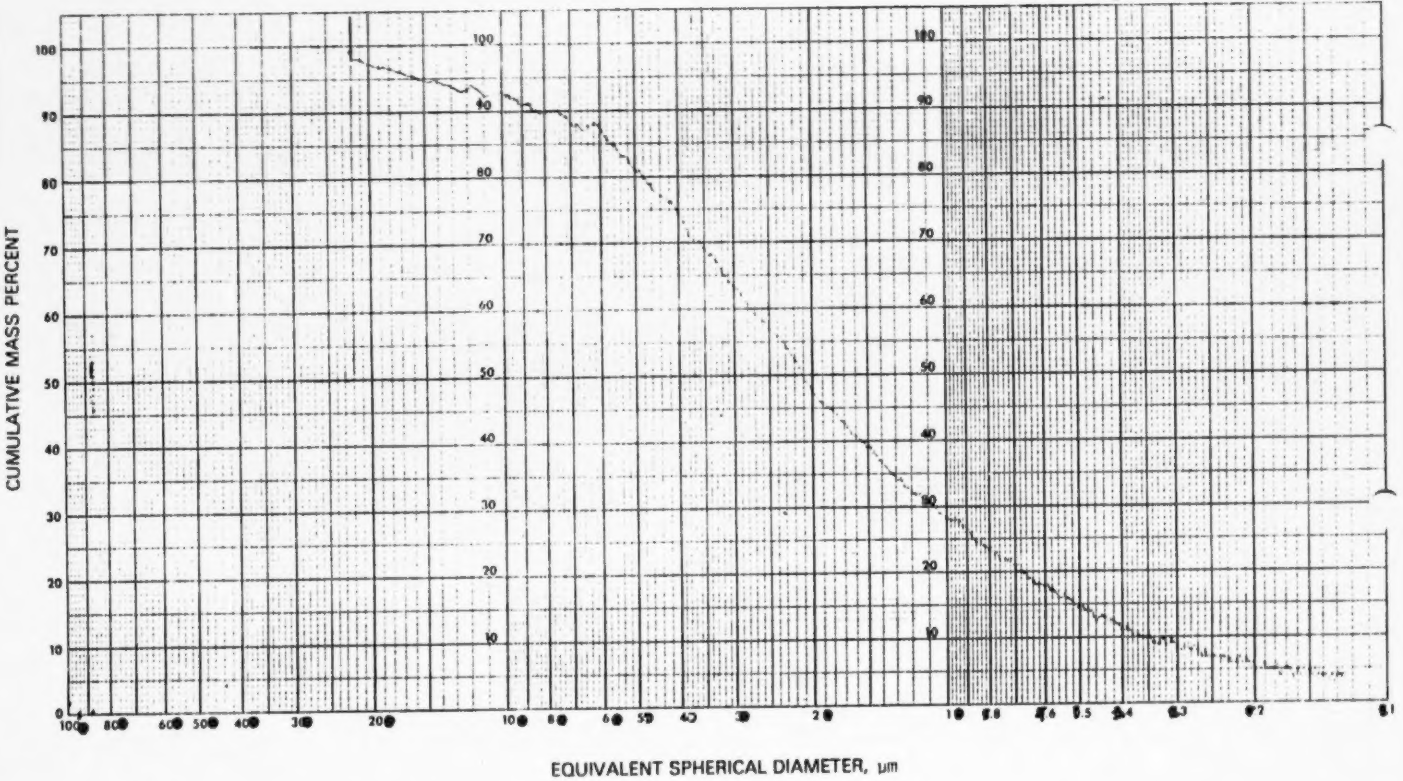
PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION **LIME SLUDGE PULLMAN KELLOGG CO.** 77-185
DATE **OCT 26,1977**

Density **2.67** g/cc LIQUID **SEDISPERSE A*13** Density **0.822** g/cc Viscosity **7.764** cp
BY **D. LONGHURST**

Preparation **10 MINUTE ULTRA-SONIC DISPERSION**
TEMPERATURE **30** °C

RATE **250** START DIA. **220** μm



micromeritics®
instrument corporation
[illegible] 30071 • USA
telephone [illegible] • telex 70-7450

```
SIEVE ANALYSIS                                                 ALLIS-CHALMERS
MATERIAL        LIME SLUDGE
SUBMITTED BY    PULLMAN KELLOGG
                HOUSTON, TEXAS
TEST NO. 77-185                                            DATE 10-25-77

A= WET-DRY DEAGGLOMERATED
B=
 SIEVE SIZE           A                  B                 C                  D
EQUIV.  ASTM     PERCENTAGE         PERCENTAGE        PERCENTAGE         PERCENTAGE
T.MESH  MU-M     ON  PASSING        ON  PASSING       ON  PASSING        ON  PASSING
  20     850     0.    100.00
  28     600      .25   99.75
  35     425      .30   99.45
  48     300      .34   99.11
  65     212      .68   98.43
 100     150     1.10   97.33
 150     106     1.95   95.37
 200      75     3.18   92.19
 270      53     2.84   89.34
 325      45     2.31   87.03
 400      38     3.25   83.78
 500      26     3.88   79.90
 PAN       0    79.90    0.
                                              A        B        C        D
80 PCT. SIZE (LOG-LOG)  =                    26
SLOPE,80% SIZE TO SMALLEST DATUM           .125
SPECIFIC GRAVITY                        *000.00
ESTIMATED SP.GR. FOR 40% VOIDS          *000.00
VOIDS FRACTION                          *000.00
BULK WEIGHT (LBS/FT**3)                 *0000.0
```

Note: This analysis probably in error due to material solubility in water.

APPENDIX B

METRIC CONVERSION CHART

METRIC CONVERSION CHART

To Convert From	To	Multiply By
atmosphere	bar	1.01325
barrel (42 US gal.)	metre^3	0.15899
British termal unit	joule	1,055.1
foot	centimetre	30.4800
foot^3/minute	decimetre^3/second	0.47195
foot^3/second	metre^3/second	0.02832
gallon US liquid	metre^3	0.00379
gallon US/hour	decimetre^3/second	0.00105
gallon US/minute	decimetre^3/second	0.06309
inch	centimetre	2.54000
inch^2	centimetre^2	6.45160
liters	centimetre^3	.00100
micron	micrometre	1.00000
milliliters	centimetre^3	1.00000
part/million (volume)	centimetre^3/metre^3	1.00000
pound mass av	kilogram	0.45359
pound mol	kilomol	0.45359
pound/force inch^2	kilopascal	6.89476
pound mass/hour	tonne/day	0.45359
pound mol	kilomol	0.45359
pound mol/hour	kilomol/hour	0.45359
°Rankine	kelvin	0.55556
revolution/minute	radian/minute	6.28319
ton mass US short	kilogram	907.185
year	annum	1.00000